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Organic Chemistry.

Preparation of $\Delta^{\alpha\gamma}$-Butadiene and its Homologues. BADISCHE ANILIN- & SODA FABRIK (D.R.-P. 252499).—When hydrogenated hydrocarbons of the benzene series containing at least one double bond are heated at high temperatures at the ordinary or (preferably) reduced pressures with an indifferent gas (such as nitrogen), they yield derivatives of butadiene. Isoprene is thus obtained from the lower-boiling fractions furnished by the decomposition of 1-methyl-Δ^1-*cyclo*hexene; or of 1-methyl*cyclo*hexan-2-ol, whilst *cyclo*hexene yields $\Delta^{\alpha\gamma}$ butadiene (erythrene), and 1-methyl-Δ^2-*cyclo*pentene furnishes piperylene, $CH_3 \cdot CH{:}CH \cdot CH{:}CH_2$.   F. M. G. M.

Preparation of Isoprene. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 251216).—When *as*-dimethylallene (b. p. 39—41°) is dropped on to strongly heated aluminium oxide, preferably under a pressure of about 20—30 mm., it is converted into pure isoprene; the aluminium oxide can be replaced by other catalytic agents, and the formation of higher polymerides must be avoided.   F. M. G. M.

Preparation of $\beta\gamma$-Dimethylerythrene. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 253081. Compare A., 1912, i, 741).— The preparation of $\beta\gamma$-dimethylerythrene by heating pinacone (1 part) with dilute sulphuric acid (10 parts) is described in the literature; it is now found that the most favourable proportions are 1 part of sulphuric acid (20%) to 10,000 parts of pinacone heated at 130—140°,

when a yield of over 70% of $\beta\gamma$-dimethylerythrene is obtained. The sulphuric acid can be replaced by methanedisulphonic or naphthalene-1 : 5-disulphonic acid.   F. M. G. M.

The History of Distillation and of Alcohol. HERMANN SCHELENZ (*Zeitsch. angew. Chem.*, 1912, **25**, 2526—2527).—Polemical against von Lippmann (A., 1912, i, 824 ; ii, 897).   C. H. D.

Preparation of Homologues of Pinacone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 251330, 251331).—The homologues of pinacone can be readily prepared in satisfactory yield by the action of aluminium amalgam on the homologues of acetone.

$\gamma\delta$-*Diethylhexane*-$\gamma\delta$-*diol*, OH·CEt$_2$·CEt$_2$·OH, m. p. 27—28°, b. p. 116—119°/17 mm., is thus obtained from diethyl ketone. $\gamma\delta$-*Dimethyl-hexane*-$\gamma\delta$-*diol*, OH·CMeEt·CMeEt·OH, b. p. 78—79°/3 mm., is prepared from methyl ethyl ketone, whilst methyl propyl ketone furnishes $\delta\epsilon$-*dimethyloctane*-$\delta\epsilon$-*diol*, OH·CMePr^a·CMePr^a·OH, m. p. 95°, b. p. 116—170°/15 mm. These reactions can be carried out in either benzene or carbon tetrachloride solutions.

II. States that magnesium and mercuric chloride in the presence of cuprous chloride can replace the aluminium amalgam in these preparations.   F. M. G. M.

The Formation of Polyatomic Rings. ADOLF FRANKE and O. KIENBERGER (*Monatsh.*, 1912, **33**, 1189—1203).—In a repetition of the work of Alberti and Smieciuszewski (A., 1906, i, 619) the authors converted $\alpha\kappa$-dihydroxydecane into the chlorohydrin, but found that the product contained also about 15% of the corresponding dichloride, and that the mixture could not be satisfactorily separated ; the constitution of the chlorohydrin was proved by re-conversion into the glycol. Heating the impure chlorohydrin with sodium hydroxide and sand gave rise to a mixture of substances of high molecular weight, but no indication of the heterocyclic isomerides, $C_{10}H_{20}O$, described earlier (*loc. cit.*).

Endeavours to prepare cyclic molecules from $\alpha\kappa$-dibromodecane (Franke and Hankam, A., 1910, i, 460) by the action of ordinary zinc dust in aqueous alcohol produced *n*-decyl alcohol, whilst the action of sodium in ether gave *n*-decane, together with a *substance*, $C_{20}H_{40}$ or $C_{20}H_{42}$, silky needles, m. p. 36°.   D. F. T.

Halogen Ethers. A. KARVONEN (*Chem. Zentr.*, 1912, ii, 1266—1271; from *Acad. Sci. Fennicae.*, A, 3, 1—103. Compare A., 1909, i, 202). The boiling points and densities have been determined for a number of carefully purified halogen ethers of the series RO·CH$_2$X, RO·CH$_2$·CH$_2$X, and RO·CH$_2$·CH$_2$·CH$_2$X, where R = H, Me, Et or Pr, and X = Cl, Br or I. They have been compared with some ethylene- and trimethylene-halogen hydrins, and with some simple alkyl haloids.

In the case of metameric halogen ethers, the removal of the halogen atom from the oxygen atom frequently causes a lowering of the boiling point, but as the molecule becomes more symmetrical with regard to the groups R and (CH$_2$)$_n$X, the boiling point rises. As the distance

of the halogen atom from the oxygen atom increases, the differences between the boiling points of the chloro- and bromo- and bromo- and iodo-compounds diminish. The difference between the boiling points of the methyl and ethyl members of a homologous series is less than that between the ethyl and propyl members. The boiling points of halogen ethers with three, four, and five members in the chain are higher than those of the corresponding alkyl haloids, but with six members in the chain the ethers boil at a lower point. The hydrins boil at higher temperatures than the halogen ethers. As for the densities, the removal of the halogen atom from the oxygen atom causes an increase in density, and the halogen ethers take a mean place between the hydrins and the alkyl haloids. In general, the simultaneous separation of two negative substituents in the molecule causes an increase in density.

General methods for the preparation and purification of these compounds are discussed. The a-halogen ethers were usually prepared by the action of the hydrogen haloid on a mixture of the alcohol with trioxymethylene (compare Litterscheid, A., 1904, i, 364); the β-chloro- and bromo-ethers by the action of the phosphorus haloid on alkyloxylated alcohols, and the γ-ethers by the action of alcohols or alcoholates on alkylene haloids, the halogenating of ethers, or by the transformation of ethers into one another. The halogen ethers are all colourless, mobile liquids. The a-ethers have pungent, aldehydic odours and fume in the air, but the β- and γ-ethers are agreeable.

The following compounds are described :

A. *a-Halogen Ethers.*—Chloromethyl ether, b. p. 59·1°/766 mm., gives a *pyridine* compound, Py,CH$_2$Cl·OMe, colourless, hygroscopic tablets ; *platinichloride*, (Py,CH$_2$Cl·OMe)$_2$PtCl$_4$, reddish-yellow needles, m. p. 189°. Bromomethyl ether, b. p. 87·2°/740·6 mm. ; *pyridine* compound, Py,CH$_2$Br·OMe, very hygroscopic powder. Iodomethyl ether, b. p. 25°/13 mm. Chloromethyl ethyl ether, b. p. 83°/763·1 mm. ; *pyridine* compound, Py,CH$_2$Cl·OEt, colourless, hygroscopic tablets ; *platinichloride*, (Py,CH$_2$Cl·OEt)$_2$PtCl$_4$, reddish-yellow prisms, m. p. 182°. *Bromomethyl ethyl ether,*

$$OEt·CH_2Br,$$

from ethyl alcohol, trioxymethylene, and hydrogen bromide, b. p. 109·2°/745·7 mm. ; *pyridine* compound, Py,CH$_2$Br·OEt, white, hygroscopic. *Iodomethyl ethyl ether*, OEt·CH$_2$I, with hydrogen iodide, b. p. 31°/11 mm. ; *pyridine* compound, Py,CH$_2$I·OEt, colourless, hygroscopic. Chloromethyl propyl ether, b. p. 109°/759·7 mm. ; *pyridine* compound, Py,CH$_2$Cl·OPr, colourless, very hygroscopic; *platinichloride*, (Py,CH$_2$Cl·OPr)$_2$PtCl$_4$, m. p. 185°. *Bromomethyl propyl ether*, OPr·CH$_2$Br, from normal propyl alcohol, trioxymethylene, and hydrogen bromide, b. p. 133·9°/744·4 mm. ; *pyridine* compound,

$$Py,CH_2Br·OPr,$$
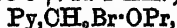
colourless, hygroscopic lamellæ. *Iodomethyl propyl ether*, OPr·CH$_2$I, with hydrogen iodide, b. p. 39°/5 mm. ; *pyridine* compound,

$$Py,CH_2I·OPr,$$
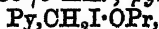
colourless.

B. *β-Halogen Ethers.*—Methyl β-chloroethyl ether,

$$OMe·CH_2·CH_2Cl,$$

by the action of phosphorus pentachloride on ethylene glycol monomethyl ether, $OMe \cdot CH_2 \cdot CH_2 \cdot OH$, and not by Fileti and Gaspari's method, b. p. 89·4°/763 3 mm. *Methyl β-bromoethyl ether*, $OMe \cdot CH_2 \cdot CH_2 Br$, from methyl β-iodoethyl ether and bromine, b. p. 110·3°/759·4 mm. Methyl β-iodoethyl ether (A., 1909, i, 202), $D_1^{20} = 1·8241$. Ethyl β-chloroethyl ether, from ethylene glycol monoethyl ether and phosphorus trichloride, b. p. 107°/751·8 mm. Ethyl β-bromoethyl ether, b. p. 40°/24 mm., from ethyl β-iodoethyl ether (*ibid*). Propyl β-chloroethyl ether, from ethylene glycol monopropyl ether and phosphorus pentachloride, b. p. 130°/756·3 mm. *Propyl β-bromoethyl ether*, $OPr \cdot CH_2 \cdot CH_2 Br$, from ethylene glycol monopropyl ether and phosphorus tribromide or hydrogen bromide, b. p. 149°/757·8 mm., 42°/11 mm. Propyl β-iodoethyl ether, $D_1^{20} = 1·5464$ (*ibid.*).

C. *γ-Halogen Ethers.*—Methyl γ chloropropyl ether, b. p. 110·4°/756·6 mm. *Methyl γ-bromopropyl ether*, $OMe \cdot [CH_2]_3 \cdot Br$, from trimethylene bromide, methyl alcohol, and zinc oxide, b. p. 132°/764·4 mm. *Methyl γ-iodopropyl ether*, $OMe \cdot [CH_2]_3 \cdot I$, from the chloroether and calcium iodide, b. p. 158—158·5°/761·8 mm. Ethyl γ-chloropropyl ether, b. p. 129°/754·7 mm. Ethyl γ-bromopropyl ether, by Noyes's method (A., 1898, i, 59), b. p. 147·8°/750 mm. *Ethyl γ-iodopropyl ether*, $OEt \cdot [CH_2]_3 \cdot I$, from the chloro-ether and calcium iodide, b. p. 172 5°/778·7 mm.

D. *Halogen Hydrins and Alkyl Haloids.*—Ethylene chlorohydrin, $OH \cdot CH_2 \cdot CH_2 Cl$, from ethylene glycol and hydrogen chloride, b. p. 129·5°/761·1 mm. Ethylene bromohydrin, $OH \cdot CH_2 \cdot CH_2 Br$, with hydrogen bromide, b. p. 45·6°/11 mm. Ethylene iodohydrin,

$$OH \cdot CH_2 \cdot CH_2 I,$$

from the chlorohydrin and sodium iodide, b. p. 61°/7 mm. Trimethylene chlorohydrin, $HO \cdot CH_2 \cdot CH_2 \cdot CH_2 Cl$, from trimethylene glycol and hydrogen chloride, b. p. 160°/734·1 mm. Trimethylene bromohydrin, $HO \cdot CH_2 \cdot CH_2 \cdot CH_2 Br$, b. p. 62°/5 mm. Trimethylene iodohydrin, $HO \cdot CH_2 \cdot CH_2 \cdot CH_2 I$, b. p. 88°/4 mm.

n-Propyl chloride, b. p. 46·6°/770·5 mm.; *n*-propyl bromide, b. p. 70·8°/769·2 mm.; *n*-propyl iodide, b. p. 101·9°/765·5 mm. *n*-Butyl chloride, b. p. 77·8°/762 7 mm.; *n*-butyl bromide, b. p. 100·2°/745·6 mm.; *n*-butyl iodide, b. p. 129·4°/746·4 mm. *n*-Amyl chloride, b. p. 105·7°/759·3 mm.; *n*-amyl bromide, b. p. 127·9°/762·4 mm.; *n*-amyl iodide, b. p. 35°/7 mm. *n*-Hexyl chloride, b. p. 132·9°/764·7 mm.; *n*-hexyl bromide, b. p. 153 4'/766·3 mm.; *n*-hexyl iodide, b. p. 51°,6 mm. J. C. W.

Preparation of Carbonic Esters. RUDOLF SCHEUBLE and A. HOCHSTETTER (D.R.-P. 252758).—*Glyceryl carbonate*, m. p. 148°, crystallises from pyridine, and is obtained in theoretical yield when anhydrous glycerol (2 parts) is heated at 140° with phenyl carbonate (7 parts) and the phenol subsequently removed in a vacuum; in this case the glycerol is fully esterified. When twice this proportion of glycerol is employed and the product extracted with a small quantity of acetone, any of the foregoing ester is left insoluble, and the acetone furnishes a complicated mixture of esters in which the glycerol is not fully esterified. These compounds can also be prepared by the action

of ethyl carbonate or carbonyl chloride on glycerol dissolved in an indifferent acid absorbing medium, and find employment in pharmacy.

F. M. G. M.

Preparation of Halogen Formyl Esters. EMANUEL MERCK (D.R.-P. 251805. Compare A., 1912, i, 877).—Chloroformyl esters can be obtained by the interaction of hydroxy-compounds with carbonyl chloride in the presence of an indifferent base or acid absorbent:

$R \cdot OH + COCl_2 = RO \cdot COCl + HCl.$

Methylhexylcarbinyl chloroformate, a colourless oil, b. p. 75°/6 mm., is obtained when a cooled benzene solution of methylhexylcarbinol (130 parts) is treated with carbonyl chloride with the subsequent slow addition of pyridine (79 parts) dissolved in 500 parts of benzene; when treated with ammonium hydroxide, it furnishes the corresponding known carbamyl ester (m. p. over 55°).

Thymyl chloroformate has b. p. 106°/10 mm., and menthyl chloroformate, b. p. 96°/5 mm.

Ethyl bromoformate, an oil with a characteristic odour, b. p. 132°/760 mm. with partial decomposition, is obtained from carbonyl bromide and ethyl alcohol in absolute ethereal solution in the presence of quinoline, whilst ethyl chloroformate is analogously prepared in the presence of methylaniline.

F. M. G. M.

Preparation of Esters of Butenol. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 252160).—When Δ^{ay}-butadienes of the general formula $CH_2 \colon CR \cdot CH \colon CH_2$ (where R is hydrogen or alkyl) are treated with a fatty acid in the presence of a condensing agent (such as sulphuric acid, zinc chloride, or potassium hydrogen sulphate), they furnish esters which are readily purified, have a characteristic odour, and on hydrolysis yield the corresponding alcohol.

Methylbutyl acetate, an oil, b. p. 100° (about), D 0·870, and saponification number 418 (about), is obtained when isoprene (100 parts), acetic acid (300 parts), and concentrated sulphuric acid (1 part) are heated together during five hours at 50°.

F. M. G. M.

The Mercury Compounds of Ethyl Nitroacetate. W. PRAGER (*Monatsh.*, 1912, **33**, 1285—1289).—The formation of ethyl mercuri-*aci*-nitroacetate anhydride, $O{<}^{NO}_{Hg}{>}C \cdot CO_2Et$, from the interaction of ammonium *aci*-nitroacetate and mercuric chloride (Scholl and Nyberg, A., 1906, i, 563), is probably preceded by the formation of a compound, $CO_2Et \cdot CH \colon NO_2 \cdot HgCl$, ethyl mercuri-*aci*-nitroacetate chloride, which, however, could not be isolated. In agreement with this idea, the yield of ethyl mercuri-*aci*-nitroacetate is increased by the addition of an equivalent quantity of sodium acetate.

The solution of ethyl mercuri-*aci*-nitroacetate in sodium hydroxide solution contains *ethyl sodium mercuri-aci-nitroacetate hydroxide*,

$CO_2Et \cdot C(\colon NO_2Na) \cdot Hg \cdot OH,$
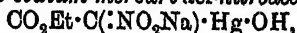
which can be obtained as a greenish-yellow substance by evaporation with exclusion of atmospheric carbon dioxide. Ethyl mercuri-*aci*-

nitroacetate anhydride dissolves also in potassium cyanide solution, forming presumably the analogous *cyanide* compound,

$$CO_2Et \cdot C(:NO_2K) \cdot Hg \cdot CN.$$
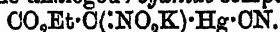
Attempts to obtain substances of analogous structure to the above from nitroacetamide, dinitromethane, and ω-nitrotoluene produced only substances of the type $CHR:NO_2 \cdot HgCl$; nitroacetamide gave a *substance*, $Hg(NH \cdot CO \cdot CH:NO_2 \cdot HgCl)_2$; the potassium derivative of dinitromethane with mercuric chloride gave yellow needles of an explosive *substance*, $NO_2 \cdot CH:NO_2 \cdot HgCl$, together with an amorphous, yellow *substance* also containing chlorine.   D. F. T.

Action of Aluminium Chloride on Acetic Anhydride. JACOB BOESEKEN and MEYER OLUWEN (*Rec. trav. chim.*, 1912, 31, 367—369).—When acetic anhydride is added to warmed aluminium chloride, acetyl chloride distils off, leaving a heavy, white precipitate of aluminium monochlorodiacetate, which forms an *additive* compound with ether, $OEt_2, 2AlCl(OAc)_2$, in large, limpid crystals.   J. C. W.

Soaps. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1912, 26, 485—495. Compare Krafft and Stern, A., 1894, i, 439, 440; Krafft and Wiglow, A., 1896, i, 80; Krafft and Strutz, A., 1896, ii, 467; Krafft, A., 1899, ii, 471, 472, 473).—When sodium palmitate is crystallised from its aqueous solution, an acid soap separates, and the mother liquor becomes alkaline. Recalculation of the data given by Krafft shows that as the sodium palmitate solution decreases in concentration, so also does the concentration of sodium hydroxide in the mother liquor, the latter value, however, finally becoming constant. This is confirmed by experiments performed by the author, who, however, contrary to Krafft, finds that fatty acids are also retained in the mother liquors.

Krafft has shown that palmitic acid may be almost completely extracted from solutions of sodium palmitate by treatment with successive quantities of toluene. The author has performed a number of experiments on the quantitative extraction of the acid by a single treatment of aqueous solutions of sodium palmitate and oleate with measured amounts of toluene, and finds that the extractability depends both on the m. p. of the acid and on its solubility in toluene. The percentage of acid extracted is inversely proportional to the concentration of sodium hydroxide in the soap solution.

The bearing of the above results on the divergent action of soap is discussed, and the conclusion drawn that this action lies rather in the power of the soap solution to emulsify the grease than in the saponification of the latter by alkali. A partly rancid fat should thus be readily emulsified by a solution of soap of suitable concentration, whilst, on the other hand, a neutral fat would first acquire the necessary acidity by extraction of a portion of the acid from the soap solution.   H. W.

Dissociation Constants of Aliphatic Hydroxy- and Alkyloxy-acids. MATTI H. PALOMAA (*Chem. Zentr.*, 1912, ii, 595—597; from *Ann. Acad. Sci. Fennicae*, 1911, *A*, 3, 1—34).—The dissociation constants of a number of aliphatic hydroxy- and alkyloxy-acids have been

determined with a view to ascertaining how this constant is affected by the positions of the oxygen atoms in the ·OH or ·OR group with respect to the carboxyl group. In general, the dissociation constant diminishes with increasing distance between the two groups, until in the δ-compounds it is nearly as low as in the normal fatty acids. Attempts to calculate the effect of distance on the specific influence of the ethereal oxygen atom by means of the equations $(y/y + 2·66)^{-\lambda} = K_0^g/K_0^g$ and $(y/y + 2 \times 2·66)^{-x} = K_5^g/K_5^g$ showed that $x = 2\cdot6$ in methoxy-compounds and 2·9 in ethoxy-compounds, the values of y being 1·45 and 1·78 respectively for the same compounds.

The following substances are described: n-*Butoxyacetic acid*, D_4^{15} 1·0256, D_4^{20} 1·0213, b. p. 113—116°/9—10 mm., K 0·0219, is a colourless liquid with a not unpleasant odour. iso*Butoxyacetic acid*, D_4^{15} 1·0117, D_4^{20} 1·0074, b. p. 114°/9 mm., K 0·0214, is a colourless liquid. α-*Ethoxypropionic acid*, b. p. 97°/11 mm., K 0·0246. β-*Methoxypropionic acid*, D_4^{15} 1·1064, D_4^{20} 1·1020, b. p. 107°/10 mm., K 0·00346. β-*Ethoxypropionic acid*, D_4^{15} 1·0508, D_4^{20} 1·0641, b. p. 119—120°/19 mm., K 0·00319. δ-*Methoxyvaleric acid*, D_4^{15} 1·0387, D_4^{20} 1·0344, b. p. 133—134°/13·5 mm., K 0·00191.   T. A H.

Action of Magnesium Methyl Iodide and Bromide on Di-α-bromoisopropyl Ketone and on α Bromoisopropyl tert.-Butyl Ketone (Pentamethylbromoacetone): Synthesis of β-Hydroxy-pentamethyl-n-valeric Acid and Pentamethylvalerolactone. (Mlle.) A. UMNOVA (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1395—1406). —Instead of the expected methylditert.-butylcarbinol, the products of the interaction of di-α-bromoisopropyl ketone, magnesium methyl iodide, and water are: (1) *isopropyl tert.-butyl ketone* (compare Nef, A., 1900, i, 349), formed from the intermediate compound,

$$CMe_3·CO·CMe_2·MgBr,$$
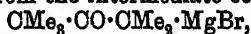
and (2) methyl*iso*propyl*tert.*-butylcarbinol (?), b. p. 65—75°/12 mm.

The action of magnesium methyl bromide on di-α-bromoisopropyl ketone yields the compound $CMe_3·CMe(OMgBr)·CMe_2·MgBr$, the latter being converted by carbon dioxide into *β-hydroxy-aaβγγ-penta-methylvaleric acid*, $CMe_3·CMe(OH)·CMe_2·CO_2H$, m. p. 128—129°, which has the normal molecular weight in boiling ether; the *silver* and *calcium* salts were analysed. Attempted oxidation of the sodium salt of the acid with potassium permanganate and subsequent distillation of the solution with sulphuric acid yields *aaββγ-pentamethyl-valerolactone*, $CMe_2 {<}^{CMe_2·O}_{CMe_2·CO}$, m. p. 59—60°, b. p. 215—220°, which has the normal molecular weight in freezing benzene; the formation of the lactone is shown to be due to the following isomeric change effected by the sulphuric acid: $CMe_3·CMe(OH)·CMe_2·CO_2H \longrightarrow OH·CMe_2·CMe_2·CMe_2·CO_2H$. β-Hydroxy-*aaββγ*-pentamethylvaleric acid may also be obtained by the action of carbon dioxide and water on the product of the interaction of magnesium methyl iodide and α-bromoisopropyl *tert.*-butyl ketone.   T. H. P.

Optically Active Dichlorosuccinic Acids. BROR HOLMBERG (*Svensk. Kem. Tid.*, 1912; Reprint, 6 pp.).—The dichlorosuccinic

anhydride obtained by the action of chlorine on a solution of maleic anhydride in carbon tetrachloride (compare Holmberg, A., 1911, i, 767 ; McKenzie, T., 1912, 101, 1196) is a mixture of a less soluble racemic dichlorosuccinic anhydride with a more soluble *meso* anhydride in the approximate proportions 5 : 1. This behaviour is in marked contrast with the oxidation of maleic acid by potassium permanganate, when the sole product is *meso*-tartaric acid. The anhydrides on treatment with cold water gave the respective acids: r-*dichlorosuccinic acid*, tablets, m. p. 173—174° (decomp.) ; meso-*dichlorosuccinic acid*, prisms, m. p. 215° (decomp.).

By fractional recrystallisation of the salt of the racemic acid with *d*-α-phenylethylamine from warm water, there was obtained d-*phenylethylamine* d-*dichlorosuccinate*, m. p. 142—142·5°, from which the pure d-*dichlorosuccinic acid*, prisms, m. p. 164—165° (decomp.), $[a]_D^{23}$ +80·41° (in ethyl acetate), could be separated by acidifying with sulphuric acid and extracting with ether. The mother liquor from the first crystallisation of the racemic salt contained a lævorotatory acid, which, when combined with *l*-phenylethylamine and crystallised from warm water, gave a salt of the same m. p. as that containing the *d*-acid and *d*-base ; the acid isolated from this salt was pure l-*dichlorosuccinic acid*, m. p. 164—165°, $[a]_D$ (in ethyl acetate) −80·38°.

The racemic acid, m. p. 173—174°, could be re-obtained by mixing equal amounts of these aenantiomorphs.   D. F. T.

New Method of Preparation of Muconic Acid. ROBERT BEHREND and GERHARD TEN DOORNKAAT KOOLMAN (*Annalen*, 1912, 394, 228—247).—Malonic acid (2 mols.) and the sodium hydrogen sulphite compound of glyoxal are boiled with water for about an hour. The solution is evaporated to a syrup, which is boiled with glacial acetic acid for about six hours, and is then treated with 36% hydrochloric acid. The sodium chloride is removed, and the filtrate is evaporated with water to a syrup. which deposits crystals after one to two days. These are treated with 95% alcohol, collected, and crystallised from hot 80% alcohol. The product is the *lactone* of *sodium hydrogen β-hydroxy-γ-sulphoadipate*,

$$\begin{matrix} CO_2H \cdot CH_2 \cdot CH\!\!-\!\!-\!\!O \\ SO_3Na \cdot CH \cdot CH_2 \end{matrix}\!\!>\!\!CO, 3\tfrac{1}{2}H_2O,$$

prismatic crystals, m. p. 270—272° (decomp.), occasionally melting at 80—85° in its water of crystallisation, re-solidifying, and melting again at 270—272°. The *lactone* of the corresponding potassium hydrogen salt, m. p 262—264° (decomp.), is obtained in a similar manner. The *lactone* of the *sodium ethyl* salt, obtained from that of the sodium hydrogen salt, boiling 95% alcohol, and 1 drop of concentrated hydrochloric acid, forms long, felted needles containing H_2O, and has m. p. 145—147° (decomp.).

By heating on the water-bath for four hours with an alkali hydroxide and a little water, the lactone of sodium hydrogen hydroxysulphoadipate is decomposed, yielding, after solution in water and acidification, about 30% of muconic acid and 60% of succinic acid.

Muconic acid has m. p. 301—305° (decomp.), and is soluble in about 5000 parts of cold water and in about 100 parts of cold absolute alcohol.

A by-product in the preparation of the lactone is a *substance*, which is isolated as the amorphous *barium* salt, $C_{10}H_{11}O_{12}SBa_2$, from which muconic acid in a yield of 38%, but not succinic acid, can be obtained by heating with an alkali hydroxide and a little water on the water-bath.

For the preparation of muconic acid there is no need to isolate the lactone. Malonic acid and the sodium hydrogen sulphite compound of glyoxal are boiled with water for an hour, the solution is evaporated to a syrup, which is heated at 140—160° until gas almost ceases to be evolved, and is then treated with an alkali hydroxide and a little water on the water-bath, as above. C. S.

Elucidation of the Constitution of Cholic Acid by Bromination. BAREND C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1912, 82, 326—341).—On bromination of cholic acid, a brown, amorphous mass is obtained, which is decomposed by sodium hydroxide, losing part of the bromine. The bromine is not completely removed on reduction either with zinc dust and alcoholic hydrogen chloride or with aluminium amalgam. Bromination in acetic acid solution is accelerated by sunlight; it is a process of substitution. The product, bromo-dehydrocholic acid, crystallises from acetic acid or from acetone in needles, decomp. 180°; when crystallised from alcohol, it forms octahedra, decomp. ±140°.

Ethyl bromodehydrocholate is obtained either by brominating ethyl dehydrocholate or by esterification of bromodehydrocholic acid. The bromine is removed quantitatively by means of sodium hydroxide from either bromodehydrocholic acid or its ester. The bromo-acid is immediately oxidised by boiling Fehling's solution or ammoniacal silver solution. Zinc dust or magnesium reduce it to dehydrocholic acid. E. F. A.

Preparation of the *p*-Bromophenylhydrazine Compound of Glycuronic Acid. ADOLF JOLLES (*Ber.*, 1912, 45, 3280—3281).—In presence of traces of impurity the crystallisation of the *p*-bromophenylhydrazine compound of glycuronic acid is prevented (Neuberg, A., 1899, i, 933). After recrystallisation of the hydrazine, the lustrous, golden-yellow needles described by Neuberg are obtained without difficulty. E. F. A.

The Action of *p*-Bromophenylhydrazine on Glycuronolactone. GUIDO GOLDSCHMIEDT and ERNST ZERNER (*Monatsh*, 1912, 33, 1217—1231).—Attempts to prepare Neuberg's compound of *p*-bromophenylhydrazine with glycuronic acid (A., 1899, i, 933), which has also been prepared and analysed by Jolles (A., 1911, i, 709), have entirely failed either when Neuberg's original directions or modifications are followed. The products actually obtained were salts of *glycuronic acid* p-*bromophenylosazone*, $CO_2H \cdot CH(OH) \cdot CH(OH) \cdot CH(OH) \cdot C(N_2H \cdot C_6H_4Br) \cdot CH:N_2H \cdot C_6H_4Br$; *sodium* salt, hygroscopic, yellow needles, m. p. 185—190°, $[a]_D$ (in alcohol and pyridine mixture) − 259° ; *barium* salt, hygroscopic, yellow

needles, m. p. 215—217° (decomp.) ; the *calcium, potassium, zinc,* and *lead* salts were also prepared.

It is suggested that the formation of the barium salt, which occurs easily and in good yield, constitutes a much more satisfactory test for glycuronic acid than does the evidently uncertain reaction of Neuberg.

<div align="right">D. F. T.</div>

The Mechanism of Oxidation Processes. OSCAR LOEW (*Ber.*, 1912, **45**, 3319).—When cuprous oxide is added to an alkaline solution of formaldehyde a vigorous evolution of hydrogen takes place, formic acid being formed. This experiment supports Wieland's idea (A., 1912, i, 944) that the oxidation of an aldehyde to an acid is a process of dehydrogenation.

<div align="right">T. S. P.</div>

aa-Bromomethylpropaldehyde. II. The Friedel - Crafts Reaction. ADOLF FRANKE and ARTUR KLEIN (*Monatsh.*, 1912, **33**, 1233—1241).—Polymeric aa-bromomethylpropaldehyde (monoclinic crystals, $a : b : c = 2\cdot6 : 1 : 4\cdot9$; $\beta = 90°7'$) only enters into synthetic reactions when the conditions are such as to cause depolymerisation (Franke, A., 1900, i, 206, 427). When treated with benzene, carbon disulphide, and aluminium chloride, hydrogen bromide is vigorously evolved and phenyl *iso*propyl ketone formed ; the oxime, tablets, m. p. 75°, with acetic anhydride yielded an *acetate,* b. p 147—149°/ 10 mm. Reduction of the ketone in aqueous alcohol by sodium amalgam gave phenyl*iso*propylcarbinol; *acetate,* b. p. 106—108°/ 9·5 mm. ; the b. p. (222—224°) of the free carbinol was considerably lower than that given earlier (Claus and Sauer, A., 1892, i, 985). Finely divided silver or copper acts on the polymeric bromomethyl-propaldehyde at 150° with the formation of *iso*butaldehyde, together with products of higher b. p.

<div align="right">D. F. T.</div>

Catalytic Reactions at High Temperatures and Pressures. XXV. VLADIMIR N. IPATIEV (*Ber.*, 1912, **45**, 3218—3226).—In addition to reduction with hydrogen under pressure in the presence of reduced nickel as catalyst, the author investigates the action of reduced palladium as catalyst. In some cases the apparatus in which the reduction was being carried out was shaken at intervals only, whilst in other cases the contents were stirred continuously by means of a stirrer actuated by a solenoid.

Reduction of β-methyl-β-ethylacraldehyde takes place at 130° in the presence of reduced nickel, but the yield of alcohol is very small, a considerable quantity of condensation products being formed. With palladium as catalyst and a hydrogen pressure of 110 atmos., reduction takes place at 110° with the formation of γ-methyl-*n*-amyl alcohol, b. p. 145—146°/758 mm., D^{18} 0·8227. The reduction takes place slowly unless continuous stirring is resorted to. Attempts to reduce the above acraldehyde in the author's apparatus, using Skita's method (A., 1909, i, 479), were unsuccessful, either at the ordinary tempera-tures or at 100°.

With palladium as catalyst, mesityl oxide is slowly reduced at 100° to methyl *iso*butyl ketone, whereas with nickel as catalyst a

mixture of methyl *iso*butyl ketone and methyl*iso*butylcarbinol is obtained at 145°.

The reduction of citral in the presence of palladium at 110°, or of a mixture of reduced nickel and nickel oxide at 140°, takes place slowly when the apparatus is continuously shaken. A mixture of products is obtained, from which $\beta\zeta$-dimethyloctane and $\gamma\eta$-dimethyloctanol were separated. When the reduction is carried out with continuous stirring, it proceeds rapidly to completion, the only product being decanol, b. p. 107—108°/12 mm., D^{18} 0.8296.

Under the same conditions as with citral, geraniol gives a mixture of decanol with small quantities of decane and condensation products when continuous shaking is resorted to, whereas with continuous stirring decanol and small quantities of decane are obtained.

At 109°, under a hydrogen pressure of 116 atmos., and in the presence of palladium as catalyst, acetylacetone is reduced to amylene $\beta\delta$-glycol, b. p. 197—198°, D^{18} 0.9602. With reduced nickel as catalyst, the reduction proceeds very slowly, the final product being a mixture of the original acetonylacetone with methyl n-propyl ketone.

By means of the apparatus with continuous stirring, the carbohydrates can readily be reduced; 20—30% aqueous-alcoholic solutions are used, the temperature being 110° with palladium as catalyst, and 130—135° with a mixture of reduced nickel and nickel oxide as catalyst; the hydrogen pressure is 100 atmos. With both catalysts, lævulose gives d-mannitol ($[\alpha]_D$ +0.71°), but the reduction is incomplete; dextrose is reduced to d-sorbitol ($[\alpha]_D$ +0.25°). Lactose is reduced to dulcitol. T. S. P.

The System Acetonephenylhydrazone-Water. JAN J. BLANKSMA (*Chem. Weekblad*, 1912, 9, 924—927. Compare Reisenegger, A., 1883, 798; Schmidt, A., 1889, 1159; Arnold, A., 1897, i, 409).— The physical data for acetonephenylhydrazone given by the investigators named are incorrect. On heating acetone with a solution of phenylhydrazine in water or dilute acetic acid, an oil is formed. When it is washed with water, dried with potassium carbonate, and distilled under reduced pressure, the product is a pale yellow liquid, b. p. 140°/16 mm., 153°/31 mm., 160°/44 mm., 163°/50 mm. Repeated solidification by cooling with a freezing mixture yielded colourless crystals, m. p. 26.6°, which on exposure to air became yellow and then brown. It forms a colourless hydrate, turned brown, and ultimately resinified by the action of air.

The author gives the fusion curves of acetonephenylhydrazone, its hydrate, and water. The solubility of the hydrate per 100 c.c. of water is 0.09 gram (0°), 0.187 gram (15°), and 0.412 gram (32.8°). A. J. W.

Syntheses by means of Mixed Organo-zinc Derivatives, α-Polychloroketones. Constitution of the Ordinary Trichloroacetone. EDMOND E. BLAISE (*Compt. rend.*, 1912, 155, 1252—1253. Compare A., 1912, i, 606).—Dichloroacetyl chloride readily condenses with α-hydroxy*iso*butyric acid to form *dichloroacetoxyisobutyric acid*, $CHCl_2 \cdot CO_2 \cdot CMe_2 \cdot CO_2H$, m. p. 95°. The corresponding *acid chloride*,

b. p. 103°/12 mm., yields an *anilide*, m. p. 99—100°, and condenses with zinc ethyl iodide, giving the *cycloacetal*, $C_5H_{12}O_3Cl_2$, m. p. 51°, b. p. 124·5—125°/16 mm., which on hydrolysis with a mixture of acetic and hydrochloric acids yields *dichloromethyl ethyl ketone*,

$$CHCl_2 \cdot COEt,$$
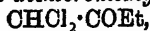
b. p. 138·5—139°. This ketone with hydroxylamine gives ethyl glyoxaldioxime, m. p. 128°. Attempts to convert the ketone into the corresponding keto-aldehyde were not successful.

Trichloroacetoxyisobutyryl chloride, b. p. 113°/18 mm, can be similarly prepared, and gives an *anilide*, m. p. 100°. The *acid* has m. p. 117°, and with zinc methyl iodide gives the *cycloacetal*,

$$C_7H_9O_3Cl_3,$$

m. p. 98—99°, which on hydrolysis yields *as-*trichloroacetone, $CCl_3 \cdot COMe$, b. p. 134°. Its *semicarbazone* crystallises in needles, m. p. 140°. Ordinary trichloroacetone, b. p. 172°, obtained by the chlorination of acetone, must therefore be the unsymmetrical compound (compare Schotterbeck, A., 1909, i, 553).   W. G.

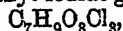## Action of Halogen Compounds of Phosphorus on Ketones : Bromo-ketones, and Keto-alcohols. ALEXEI E. FAVORSKI (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1339—1395).

—According to Henry (*Ber.*, 1875, 8, 400) the action of phosphorus pentachloride on diisopropyl ketone results in replacement of the carbonylic oxygen by two atoms of chlorine, the compound thus formed giving $\beta\delta$-dimethyl-$\Delta^{\beta\gamma}$-penta-diene when treated with alcoholic potassium hydroxide. The author finds, however, that the principal product of this action is not a dichloro-compound, but *isopropyl* α-chloro*isopropyl* ketone,

$$CMe_2Cl \cdot CO \cdot CHMe_2.$$
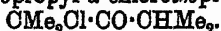
Further, in the case of *isopropyl tert.*-butyl ketone, the reaction proceeds similarly, α-chloro*isopropyl tert.*-butyl ketone being mainly obtained. With phosphorus pentabromide, the reaction takes place in the above direction with all ketones, and of a number of these compounds examined, only pinacolin underwent to some extent replacement of its carbonylic oxygen by two bromine atoms.

The ability of the carbonyl group of a ketone to react with phosphorus pentahaloid depends on the structure of the ketone and on its greater or less capacity to undergo enolisation. Ketones of normal structure (mono- and di-substituted acetones) readily react in the cold with phosphorus pentachloride by means of their carbonyl group, the oxygen of which is replaced by chlorine. On the other hand, such ketones as diisopropyl ketone, and, more especially *isopropyl tert.*-butyl ketone, react with phosphorus pentachloride only in the hot, when they undergo enolisation, the action of the chlorine liberated by dissociation of the pentachloride resulting in the formation of a mono-chloroketone :

(1) $CMe_2:O + PCl_5 = CMe_2Cl \cdot OPCl_4 = POCl_3 + CH_3 \cdot CCl_2 \cdot CH_3$;

(2) $CHMe_2 \cdot CO \cdot CHMe_2 \longrightarrow CMe_2:C(OH) \cdot CHMe_2 + Cl_2 =$
$$CMe_2Cl \cdot CO \cdot CHMe_2 + HCl.$$
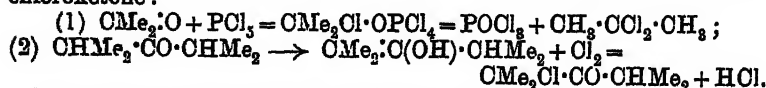
Phosphorus pentabromide dissociates more readily, both on heating and in solution, than the pentachloride, and exerts, therefore, increased enolising action on the ketones, which yield mainly bromoketones :

$CMe_2{:}O \longrightarrow CH_3{\cdot}C(OH){:}CH_2 + Br_2 = CH_3{\cdot}CO{\cdot}CH_2Br + HBr$. Experiment shows, indeed, that the action of bromine on ketones yields the same products as that of phosphorus pentabromide, the latter, however, acting more vigorously owing to the enolising action of the bromine formed on dissociation of the pentabromide being more energetic than the action of free bromine; for instance, *iso*propyl α-bromo*iso*propyl ketone is not acted on by bromine, but is converted into the dibromo-derivative when heated with phosphorus pentabromide on a water-bath.

The first bromine atom enters the ketone molecule in the α-position with respect to the carbonyl group and mostly replaces a hydrogen atom of the less highly hydrogenated hydrocarbon group. The second bromine atom proceeds mostly to the same carbon atom as the first, so that unsymmetrical αα-dibromoketones are obtained in preponderating amount. If, however, the first bromine atom replaces the only hydrogen atom combined with the first of the α-carbon atoms, the second bromine atom becomes united with the other carbon atom adjacent to the carbonyl group, symmetrical dibromoketones being obtained. Tribromoketones may also be formed by the replacement of all three hydrogen atoms united to the carbon atoms in the α-positions.

[With I. IDELSON and (Mlle.) A. UMNOVA.]—iso*Propyl* α-*chloro*iso*propyl ketone*, $CMe_2Cl{\cdot}CO{\cdot}CHMe_2$, is a colourless liquid, b. p. 142°/760 mm., 92°/150 mm., D_0^0 0·9800, D_0^{20} 0·9592, giving no compound with semicarbazide. By alcoholic potassium hydroxide it is converted into iso*butyryldimethylcarbinol*, $OH{\cdot}CMe_2{\cdot}CO{\cdot}CHMe_2$, which is a colourless liquid with an odour like that of camphor, b. p. 164·5—165°/761 mm., D_0^0 0·9408, D_0^{20} 0·9239, and forms a *semicarbazone*, $C_8H_{17}O_2N_3$, m. p. 196°, in either aqueous or alcoholic solution (compare Kling, A., 1905, i, 503). Reduction of the keto-alcohol yields : (1) βγ-dihydroxy-βδ-dimethylpentane, $OH{\cdot}CMe_2{\cdot}CHPr^\beta{\cdot}OH$, m. p. 59°, and (2) di*iso*-propylcarbinol. Conversion of di*iso*propylcarbinol into the corresponding γ-iodo-βδ-dimethylpentane, $CHMe_2{\cdot}CHI{\cdot}CHMe_2$, and treatment of the latter with alcoholic potassium hydroxide yields βδ-*dimethyl*-Δ*β-amylene*, $CMe_2{:}CHPr^\beta$, b. p. 82—84°, oxidation of which gives *iso*butyryldimethylcarbinol (see above) (compare Blaise and Herman, A., 1910, i, 534).

[With E. FRICMAN.]—iso*Propyl* tert.-*butylcarbinol*,

$$OH{\cdot}CHPr^\beta{\cdot}CHMe_3,$$

obtained by the action of magnesium *tert.*-butyl chloride on *iso*but-aldehyde, is a liquid, b. p. 150—151°/760 mm., D_0^0 0·8479, D_0^{10} 0·8298, m. p. − 13°, with a camphor-like odour. On oxidation it yields *iso*-*propyl* tert.-*butyl ketone*, $COPr^\beta{\cdot}CHMe_3$, which is a mobile liquid, b. p. 134—135°/760 mm., D_0^0 0·8240, D_0^0 0·8065, with an intense camphor-like odour; neither the hydrazone nor the semicarbazone could be obtained. Treatment of the ketone with phosphorus pentachloride in a sealed tube at 140° gives : (1) α-*chloroiso*propyl tert.-*butyl ketone*, $CMe_2Cl{\cdot}CO{\cdot}CMe_3$, b. p. 79—110°/18 mm., which yields Butlerov's oxoctenol, $\begin{smallmatrix}CMe_2\\O\end{smallmatrix}{>}C(OH){\cdot}CMe_3$ (A., 1882, 936), on treatment with

potassium hydroxide solution; (2) $\gamma\gamma$-*dichloro-$\beta\beta\delta$-trimethylpentane*, CMe$_3$·CCl$_2$·CHMe$_2$, b. p. 122—125°/19 mm.

[With B. ISATSCHENKO.]—The action of phosphorus pentabromide on acetone yields bromoacetone, and that of the pentabromide or bromine (1 mol.) on methyl ethyl ketone gives *methyl α-bromoethyl ketone*, which is a liquid, b. p. 35—38°/12 mm., D$_{20}^{20}$ 1·4380. With 2 mols. of bromine, methyl ethyl ketone yields (1) *bromomethyl α-bromoethyl ketone*, CH$_2$Br·CO·CHMeBr, b. p. 194—195°, 80—83°/ 10 mm., D$_{20}^{20}$ 1·9729; (2) a tribromo-derivative of the ketone.

[With A. VANSCHEJDT.]—The action of phosphorus pentabromide on methyl *iso*propyl ketone yields: (1) *Methyl α-bromoisopropyl ketone*, CH$_3$·CO·CMe$_2$Br, b. p. 49°/22 mm., 139°/760 mm., D$_4^{20}$ 1·3377, which is converted into acetyldimethylcarbinol (compare Diels and Johlin, A., 1911, i, 254) when heated in a sealed tube with potassium formate at 130° (compare Kling, A., 1905, i, 503); the *acetyl* derivative of the carbinol, C$_7$H$_{12}$O$_3$, b. p. 65°/15 mm., 170—171°/ 760 mm., forms the *oxime*, C$_7$H$_{13}$O$_3$N, m. p. 102—103°. (2) *Bromomethyl α-bromoisopropyl ketone*, CH$_2$Br·CO·CMe$_2$Br, which is best obtained by the action of bromine on the preceding compound, and is a colourless liquid, b. p. 99°/18 mm., m. p. 10°, D$_{20}^{20}$ 1·830, yielding no crystalline products with hydroxylamine, phenylhydrazine, or semicarbazide. With alcoholic potassium hydroxide (compare Favorski, A., 1895, i, 496; Semenov, *J. Russ. Phys. Chem. Soc.*, 1911, 48, 693) it yields $\beta\beta$-dimethylacrylic acid (compare Weinig, A., 1895, i, 17). (3) *Dibromomethyl α-bromoisopropyl ketone*, CHBr$_2$·CO·CMe$_2$Br, which forms colourless, silky needles, m. p. 52°, b. p. 110—115°/6 mm., D$_{21}^{22}$ 2·051, D$_{21}^{22}$ 2·268. By aqueous potassium hydroxide, this ketone is converted into $\beta\beta$-dimethylglyceric acid, OH·CMe$_2$·CH(OH)·CO$_2$H, the *iso*butyl ester of which, C$_9$H$_{18}$O$_4$, is a viscous liquid, b. p. 230° (decomp.), 121°/11 mm., D$_{21}^{21}$ 1·0774, D$_4^{21}$ 1·0752. When distilled in presence of sulphuric acid, $\beta\beta$-dimethylglyceric acid yields α-hydroxy-*iso*butaldehyde. These three bromo-ketones are also obtainable from methyl *iso*propyl ketone by the action of bromine, which gives, in addition, a *tetrabromo*-derivative, C$_5$H$_6$OBr$_4$, b. p. 157°/27 mm., D$_{21}^{21}$ 2·446.

[With T. VELITSCHKOVSKI.]—The action of phosphorus pentabromide on pinacolin yields: (1) *Bromomethyl tert.-butyl ketone*, CH$_2$Br·CO·CMe$_3$, which is a liquid with a pungent odour, b. p. 70—73°/9 mm., D$_0^{20}$ 1·3274, D$_0^0$ 1·3508, and reduces Fehling's solution in the cold. When heated with water and freshly-precipitated barium carbonate, it yields *hydroxymethyl tert.-butyl ketone*, OH·CH$_2$·CO·CMe$_3$, which is a liquid, b. p. 158—160°, 52·5°/12 mm., m. p. +9·5°, D$_{20}^{20}$ 0·95295, D$_0^0$ 0·95164, D$_0^{13\cdot5}$ 0·9576, and yields an *oxime*, C$_6$H$_{13}$O$_2$N, m. p. 89—90°, and a *phenylosazone*, C$_{18}$H$_{22}$N$_4$, m. p. 119—120°. Oxidation of this keto-alcohol yields first the corresponding keto-aldehyde and then α-hydroxy-$\beta\beta$-dimethylbutyric acid, CO$_2$H·CH(OH)·CMe$_3$. (2) Dibromomethyl *tert.*-butyl ketone, CHBr$_2$·CO·CMe$_3$ (compare Kondakov, A., 1899, i, 859; Wittorv, A., 1900, i, 421). (3) *$\beta\beta$-Dibromo-$\gamma\gamma$-dimethylbutane*, CH$_3$·CBr$_2$·CMe$_3$, m. p. 191—191·5°.
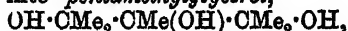
[With D. Sciborski.]—The action of phosphorus pentabromide on ethyl *isopropyl* ketone yields: (1) *Ethyl α-bromoisopropyl ketone,* $CBrMe_2 \cdot COEt$, b. p. 50—53°/13 mm., D_1^{20} 1·2847, D_1^{0} 1·3098, which gives *ethyl α-hydroxyisopropyl ketone,* $OH \cdot CMe_2 \cdot COEt$, b. p. 95—97°/100 mm., D_4^{0} 0·9548, D_4^{20} 0 9446, D_0^{20} 0·9405, when heated with water and freshly-precipitated barium carbonate, and (2) *α-bromoethyl α-bromoisopropyl ketone,* $CHMeBr \cdot CO \cdot CMe_2Br$, b. p. 80—81°/13 mm.

[With P. Aschmarin.]—*Ethyl*tert.-*butylcarbinol,* $OH \cdot CHEt \cdot CMe_3$, obtained by the interaction of magnesium *tert.*-butyl chloride and propaldehyde, is a liquid, b. p. 132—135°, 42—44°/15 mm., D_4^{0} 0·84078, D_4^{20} 0·82462. It forms an *acetyl* derivative, $C_9H_{18}O_2$, b. p. 157—159°/770 mm., and on oxidation yields *ethyl* tert.-*butyl ketone,* $CMe_3 \cdot COEt$, b. p. 125—126°/769 mm., D_4^{0} 0·8303, D_4^{20} 0·8125, which gives a *semicarbazone,* $C_8H_{17}ON_3$, m. p. 144°. The action of phosphorus pentabromide on this ketone yields: (1) *α-Bromoethyl* tert.-*butyl ketone,* $CHMeBr \cdot CO \cdot CMe_3$, b. p. 67·5—68·5°/11 mm., D_4^{0} 1·2687, D_4^{20} 1·2456, and (2) *αα-dibromoethyl* tert.-*butyl ketone,* $CMeBr_2 \cdot CO \cdot CMe_3$, m. p. 77·5—79°/10 mm., D_4^{0} 1·5955, D_4^{20} 1·5674. *Trimethylacetylmethylcarbinol,* $OH \cdot CHMe \cdot CO \cdot CMe_3$, obtained by way of its *acetyl* derivative, $OAc \cdot CHMe \cdot CO \cdot CMe_3$, b. p. 189—191°, from α-bromoethyl *tert.*-butyl ketone, is a liquid, b. p. 100—101·5°/100 mm., D_4^{0} 0·9483, D_4^{20} 0·9301, with a faint camphor-like odour and yields a *semicarbazone* in two modifications, m. p. 98—100° and 135° respectively.

[With (Mlle.) A. Umnova.]—The action of bromine on di*iso*propyl ketone yields *isopropyl α-bromoisopropyl ketone,* $CMe_2Br \cdot CO \cdot CHMe_2$, b. p. 166—168°, 50—51°/10 mm., D_0^{0} 1·2763, D_0^{20} 1·2636, which is converted by phosphorus pentabromide into *di-α-bromoisopropyl ketone,* $CO(CMe_2Br)_2$, a yellow liquid with an odour of camphor, b. p. 84—85°/9 mm., D_0^{0} 1·6441, D_0^{20} 1·6174. *Di-α-hydroxyisopropyl ketone,* $CO(CMe_2 \cdot OH)_2$, obtained by the action of aqueous potassium hydroxide on the dibromo-ketone, forms rhombic plates, m. p. 42—43°, b. p. 101·5—102°/11 mm., gives a *diacetyl* derivative, $C_{11}H_{18}O_5$, m. p. 51—52°, and is converted by magnesium methyl iodide and water into *pentamethylglycerol,*

$$OH \cdot CMe_2 \cdot CMe(OH) \cdot CMe_2 \cdot OH,$$

which crystallises in slender, shining needles or prisms, m. p. 118—119°. When heated with 2% sulphuric acid solution, the trihydric alcohol decomposes into acetone and methyl *iso*propyl ketone.

[With G. Briliant.]—The action of phosphorus pentabromide on *iso*propyl *tert.*-butyl ketone yields *α-bromoisopropyl* tert.-*butyl ketone,* $CMe_3 \cdot CO \cdot CMe_2Br$, b. p. 91—93°/40 mm., 62—64°/12 mm., D_0^{0} 1·2441, D_0^{20} 1·2233, which gives a good yield of Butlerov's oxoctenol (see above) when heated with 10% aqueous potassium hydroxide.

[With (Mlle.) A. Zacharova.]—iso*Propylisobutylcarbinol,*

$$CHMe_2 \cdot CH(OH) \cdot CH_2 \cdot CHMe_2,$$

obtained by the action of magnesium *iso*butyl bromide on *iso*but-aldehyde, has b. p. 156°, D_0^{0} 0·8325, D_0^{20} 0·8222, and on oxidation yields *iso*propyl *iso*butyl ketone, $CHMe_2 \cdot CO \cdot CH_2 \cdot CHMe_2$, b. p. 147—148°, D_0^{0} 0·82705, D_0^{20} 0·81223. *α-Bromoisopropyl* isobutyl ketone, $CMe_2Br \cdot CO \cdot CH_2 \cdot CHMe_2$, obtained by the action of either bromine or

phosphorus pentabromide, has b. p. 75—78°/12 mm., 81—85°/21 mm., D_0^0 1·2187, D_0^{2J} 1·1979, and, when heated with potassium formate and methyl alcohol in a sealed tube at 120°, yields iso*butyryldimethyl-carbinol*, OH·CMe$_2$·CO·CH$_2$·CHMe$_2$, b. p. 67—70°/13 mm., D_0^0 0·9159, D_0^{u0} 0·8962, the *semicarbazone* of which, $C_9H_{19}O_2N_3$, m. p. 126°, was prepared ; oxidation of the keto-alcohol gives valeric acid.* *a-Bromo-*iso*propyl a-bromo*iso*butyl ketone*, CMe$_2$Br·CO·CHBr·CHMe$_2$, b. p. 103—105°/21 mm., is also formed by the action of phosphorus pentabromide on *iso*propyl *iso*butyl ketone.

[With N. MANDRYK.]—*Phenyl*iso*propylcarbinol*, OH·CHPh·CHMe$_2$, prepared by the action of magnesium *iso*propyl⁵ iodide on benzalde-hyde, has b. p. 110—111°/13 mm., D_0^0 0·9933, D_{20}^{20} 0·9790, forms the *acetyl* derivative, $C_{12}H_{16}O_2$, b. p. 118—120°/16 mm., and on oxidation yields *phenyl* iso*propyl ketone*, CHMe$_2$·COPh, which is a colourless liquid, b. p. 95—98°/10 mm., D_0^0 0·9996, D_0^{20} 0·9848, and forms the *semicarbazone*, $C_{11}H_{15}ON_3$, m. p. 166—167°. The action of phosphorus pentabromide on the ketone yields phenyl a-bromo*iso*propyl ketone, b. p. 129—130°/12 mm., D_0^0 1·3845, D_{20}^{20} 1·3652 (compare Collet, A., 1898, i, 477). *Benzoyldimethylcarbinol*, CMe$_2$Bz·OH, b. p. 116—118°/9 mm., D_0^0 1·0928, D_{20}^{20} 1·0775, when kept in a sealed tube for some months, forms the *compound*, CMe$_2$Bz·O·CMe$_2$Bz or

$$\underset{CMe_2}{\overset{O}{>}}CPh·O·CPh\underset{CMe_2}{\overset{O}{<}},$$
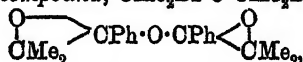
m. p. 185—186°.

[With (Mlle.) L. KOLOTOVA.]—The action of phosphorus penta-bromide on *cyclo*hexyl methyl ketone yields *bromocyclohexyl methyl ketone*, CBrAc$\underset{CH_2·CH_2}{\overset{CH_2·CH_2}{<}}CH_2$, b. p. 97—101°/13 mm., and this, with heated with aqueous potassium hydroxide, gives 1-*acetyl-cyclohexan-1-ol*, C_6H_{10}Ac·OH, b. p. 92—94°/18 mm., D_0^0 1·04259, D_0^{20} 1·02569, which forms the *semicarbazone*, $C_9H_{17}O_2N_3$, m. p. 102° (decomp.), but does not yield a phenylosazone or react with Fehling's solution. On oxidation, 1-acetyl*cyclo*hexan-1-ol yields *cyclo*hexanone and acetic acid.

[With M. CHARITONOVA.]—The action of phosphorus pentabromide on *cyclo*hexyl *iso*propyl *ketone*, C_6H_{11}·CO·CHMe$_2$, b. p. 83°/11 mm., which was prepared from magnesium *cyclo*hexyl bromide and *iso*but-aldehyde, yields *cyclohexyl a-bromoisopropyl ketone*, C_6H_{11}·CO·CMe$_2$Br, b. p. 111—112°/10 mm., m. p. 29°. On oxidation, the latter gives *cyclohexyl a-hydroxyisopropyl ketone*, C_6H_{11}·CO·CMe$_2$·OH, b. p. 97—98°/11 mm., D_0^0 0·9764, D_0^{20} 0·9655, the *semicarbazide* of which, $C_{11}H_{21}O_3N_3$, m. p. 183°, was prepared. Oxidation of the keto-alcohol yields hexahydrobenzoic and acetic acids.   T. H. P.

Sugar Solutions and Calcium Hydroxide. P. J. H. VAN GINNEKEN (*Zeitsch. ver. deut. Zuckerind*, 1912, 1293—1295).—Polemical. A reply to the criticisms of Weisberg (A., 1912, i, 608).   E. F. A.

Photolysis of Sucrose by Ultra-violet Rays. DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1912, 155, 1016—1018. Compare A., 1910, ii, 813, 814; 1912, i, 750).—Working with rays ($\lambda = 0\cdot25\mu$)

the photolysis of sucrose can be shown to take place in two stages, the first, lasting six hours and consisting of hydrolysis of the sucrose to dextrose and lævulose, the solution remaining neutral, and no gas being evolved; and the second, of the decomposition of these two hexoses with the evolution of carbon monoxide and hydrogen, the relative volumes of these gases liberated pointing to the more rapid decomposition of the lævulose than the dextrose. With the extreme ultra-violet rays the first stage is very rapid, and the separation of the two phases is somewhat difficult. W. G.

Composition of Press Cakes from Sugar Refineries. Léon Lindet and Charpentier (*Bull. Soc. chim.*, 1912, [vi], 11, 956—958). —It is shown that these cakes, after having been properly washed by the slightly ammoniacal water produced by condensing steam from the evaporating pans, contain no free lime. The sugar, which can be extracted by washing them with water, is present in the free state. The cakes always contain insoluble tribasic calcium saccharate, owing to the fact that this compound is not decomposed in the customary rapid treatment with carbon dioxide. T. A. H.

Plant Colloids. II. The Stability of Starch Solutions. Max Samec (*Koll. Chem. Beihefte*, 1912, 4, 132—174. Compare A., 1912, ii, 144).—The ageing of starch solutions is accompanied by a very considerable reduction of the viscosity, and the influence of foreign substances on the changes which occur during the process of ageing has been investigated by means of viscosity measurements. The same starch was used for all the experiments, and the solutions prepared by mixing a weighed quantity of the starch to a paste with 25 c.c. of cold water and then adding the paste to 75 c.c. of boiling water. After boiling for one minute, the starch paste was heated for two hours at 120° and then filtered under pressure, the age of the starch solution being reckoned from the time of the completed filtration.

The rate of diminution of the viscosity of such starch solutions is greater for dilute than for more concentrated solutions. It is also greater for solutions which have been shaken than for corresponding solutions which have been kept undisturbed. The addition of hydrochloric acid diminishes the initial viscosity, but retards the further progress of the change, and thus increases the stability of the solutions. With increasing concentration of the acid, the influence on the stability increases at first and passes through a maximum. Potassium hydroxide raises the viscosity when added in very small quantity; if larger amounts are present the viscosity is diminished, however, and this effect is very pronounced in the case of solutions which contain alkali hydroxide in more than $0.001N$-concentration. Ammonium sulphate and ammonium thiocyanate both diminish the initial viscosity, but in concentrated solution the influence of the two salts on the stability of the starch solution is quite different, in that the sulphate increases the stability, whilst the thiocyanate is comparatively inactive.

The viscosity change is irreversible in character, and the sensitiveness of the starch solutions towards electrolytes diminishes with the time which has elapsed since their preparation. The ageing of the

solutions is also found to be accompanied by an increase in the electrical conductivity.

An explanation of some of the observed facts is suggested, in which the author assumes that the active constituent is a complex compound of starch and phosphoric acid.   H. M. D.

Photochemical Synthesis of Carbohydrates. JULIUS STOKLASA JOHANN ŠEBOR, and WENZEL ZDOBNICKÝ (*Biochem. Zeitsch.*, 1912, 47,. 186—188. Compare A., 1912, i, 606).—A reply to the criticisms of Walther Löb (A., 1912, i, 750).   S. B. S.

Existence of a Hydrate of Nitrocellulose. TH. CHANDELON (*Bull. Soc. chim. Belg.*, 1912, 26, 495—502).—The viscosities of solutions of dry and moist nitrocelluloses in mixtures of alcohol and ether have been examined, together with the viscosities of solutions of dry nitrocellulose in the same mixture to which small quantities of water have been added.

The author is led to the conclusions : (1) that the greater solubility of moist nitrocellulose in a mixture of alcohol and ether does not depend on the existence of a hydrate, but simply on the dilution of the solvent by the water contained in the moist substance ; (2) that it is im-material whether this water is contained in the moist nitrocellulose or previously added to the solvent, and (3) that a mixture of alcohol and ether which contains small quantities of water has a solvent action towards nitrocellulose superior to that of an anhydrous mixture of the two solvents.   H. W.

A New Nitrocellulose. TASSART (*Bull. Soc. chim.*, 1912, [iv], 11, 1009—1011).—By the successive action of sulphuric acid and nitric acid on cotton with avoidance of rise in temperature, the author has obtained a white, powdery unstable compound which is provision-ally termed α-nitrocellulose and which contains about 13·5% nitrogen. When heated on the water-bath it becomes pasty, evolves nitrous fumes with increasing intensity, and ultimately ignites. In thin layers, however, heating can be conducted without inflammation, when the residue, after cessation of evolution of nitrous fumes, is found to contain 6% nitrogen and to reduce Fehling's solution. The latter property is not possessed by α-nitrocellulose to any marked extent.

Certain substances, such as diphenylamine, dextrose, diaminophenol hydrochloride, α-naphthylamine, tetramethyldiaminobenzophenone, etc., when warmed with α-nitrocellulose on the water-bath cause darkening and subsequent charring without evolution of nitrous fumes or inflammation. On the other hand, the tendency of α-nitro-cellulose towards spontaneous inflammability is accentuated by the presence of p-phenylenediamine.

α-Nitrocellulose is insoluble in water, soluble in methyl and ethyl alcohols, aldehyde, and acetone. Treatment with water or aqueous sodium hydroxide leaves it unaffected, but alcoholic sodium hydroxide causes marked alteration in properties, and renders it completely soluble in water.

Dextrose and amidon, when similarly treated with sulphuric and nitric acids, yield similar products.   H. W.

Formylated Cellulose. EDWARD C. WORDEN (*J. Soc. Chem. Ind.*, 1912, **31**, 1064—1068).—The author discusses at some length the several methods of preparing cellulose acetates and formates which have been published, also the means which have been devised for converting these esters into plastic substances resembling celluloid.

Results of work carried out with the object of converting cellulose formate, obtained by the action of formic acid (99%) and zinc chloride on a cellulose prepared by denitrating nitro-cellulose with ammonium sulphide solution, into a modification having more valuable properties, such as greater solubility in common organic solvents, are recorded.

The crude solutions of cellulose formate as obtained directly from the cellulose were treated with small quantities of water for varying periods. Generally speaking, the effect of this treatment is to increase the solubility of the product in solvents such as acetone, chloroform, and tetrachloroethane, the solubility becoming greater as the proportion of water employed or the period of treatment is increased. W. H. G.

Neurine Bromide. ERNST SCHMIDT and A. SEEBERG (*Apoth. Zeit.*, 1912, **71**; Reprint, 2 pp.).—The conversion of large quantities of trimethylbromoethylammonium bromide into neurine by moist silver oxide is often accompanied by serious loss, due to the formation of trimethylamine. A cheaper and more satisfactory method is described, in which barium hydroxide is used in place of silver oxide.

Neurine bromide on heating with hydrobromic acid at 165—170° gives, as already observed, trimethyl-β-bromoethylammonium bromide, but the mother liquors contain another substance, apparently the isomeric *trimethyl-a-bromoethylammonium bromide*, crystallising in tablets. D. F. T.

The Asymmetric Cobalt Atom. VI. ALFRED WERNER and McCUTCHEON (*Ber.*, 1912, **45**, 3281—3287).—The active compounds of cobalt which have hitherto been prepared belonging to the series $[en_2CoX_2]X$ contain two monobasic acid residues in direct combination with the cobalt atom, for example, $[Cl_2Co\ en_2]X$ and $[(NO_2)_2Co\ en_2]X$. The authors have now investigated the compounds in which the two X-groups have been replaced by one dibasic acid residue, for example, the oxalic and carbonic acid residues, in order to see if they show mirror-image isomerism. These compounds have

the following structural formulæ : $\left[\begin{matrix} O:C\cdot O \\ O:C\cdot O \end{matrix}\!\!>\!Co\ en_2\right]X$ and

$$\left[O:C\!\!<^O_O\!\!>\!Co\ en_2\right]X.$$
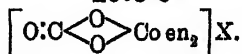
It has been shown previously (A., 1912, i, 78) that geometrical isomerides do not exist, and that the acid residues occupy neighbouring co-ordination positions. Optical isomerides should, however, exist in accordance with the following scheme :
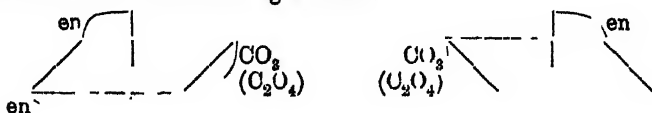
It was not found possible to resolve the inactive compounds into their active components, but the individual isomerides have been obtained directly from the active 1:2-dichlorodiethylenediaminecobaltic salts by the action of potassium carbonate and oxalate respectively, for example : $[Cl_2Co\ en_2]Cl + K_2CO_3 = [CO_3Co\ en_2]Cl + 2KCl$. The fact that such active isomerides have been prepared forms further support for the *cis*-structure of these compounds.

The active carbonato-salts possess an intense red colour, so that their rotatory power could only be determined for red light (C line). The observed specific rotations are fairly large, for example, the chloride has $[a]_c \pm 350°$, and it is noteworthy that the various salts show very different rotatory powers, the iodide having $[a]_c \pm 250°$ and the dithionate $[a]_c \pm 216°$. In cold aqueous solution the salts are fairly stable, undergoing racemisation very slowly, the rotation diminishing by one-half in about eight days. At 90° racemisation is complete in a short time. The products of racemisation consist of the inactive carbonato-salts, and are formed probably by one of the valencies of the carbonato-residue becoming loosened for a time, the radicle $[Co\ en_2]$ then undergoing a structural change.

The oxalo-salts possess a smaller specific rotation than the carbonato-salts, the chloride and nitrate having $[a]_c \pm 200°$ and the iodide $[a]_c \pm 160°$. They are quite stable, the aqueous solutions showing no tendency to racemise even on warming.

The sign of rotation of the various carbonato- and oxalo-salts is the opposite to that of the dichloro-salts from which they are obtained.

Carbonato-salts, YX, where $Y = [CO_3Co\ en_2]$.—The d- and l-*chlorides*, YCl, are obtained by heating a mixture of 1 gram of the active dichloro-chloride with the calculated quantity of potassium carbonate and 0·5 c.c. of water on the water-bath until the colour changes to red (2 mins.) The reaction product is then rapidly cooled in a freezing mixture and rubbed with a platinum spatula, when the chloride separates as a red, crystalline powder, forming a mixture of the active and racemic compounds. The racemate is less soluble than the active salt, and is left undissolved when sufficient water is added to dissolve about three-quarters of the solid. The pure active chloride is then obtained from the aqueous solution by precipitation with a mixture of alcohol and ether. $[a]_c \pm 350°$, $[M]_c \pm 960°$; 100 c.c. of water dissolve 5 grams of the active chloride at 18°.

The active *iodides*, YI, and *dithionates*, $Y_2S_2O_6$, were obtained from the active chlorides by double decomposition with ammonium iodide and sodium dithionate respectively. The former have $[a]_c \pm 250°$, $[M]_c \pm 915°$, and dissolve to the extent of 1 gram in 100 c.c. of water at 18°; the latter has $[a]_c + 216°$ and $- 220°$, $[M]_c + 689°$ and $- 702°$, the solubility being 3·5 grams of the salt in 100 c.c. of water at 18°.

Oxalo-salts, YX, where $Y = [C_2O_4Co\ en_2]$.—The active *chlorides*, YCl,H$_2$O, are prepared similarly to the carbonato-salts, using potassium oxalate, the chief difference being that the racemate is more soluble than the active salt, the latter separating out fairly pure. $[a]_c + 200°$ and $- 204°$, $[M]_c + 641°$ and $- 653°$; 100 c.c. of water

dissolve 2 grams of the salt at 18°. The active *iodides*, YI, and *nitrates*, YNO_3,H_2O, were obtained from the chloride by double decomposition with ammonium iodide and silver nitrate respectively. Their solubilities are respectively 1 gram and 4 grams in 100 c.c. of water at 18°. The former have $[a]_c + 160°$ and $- 155°$, $[M]_c + 630°$ and $- 610°$, the latter having $[a]_c + 204°$ and $- 200°$, $[M]_c + 689°$ and $- 676°$.

<div align="right">T. S. P.</div>

The Asymmetric Cobalt Atom. VII. ALFRED WERNER and YUJI SHIBATA (*Ber.*, 1912, **45**, 3287—3293).—Optically active 1 : 2-diamminediethylenediaminecobaltic salts have now been obtained. They could not be prepared by resolution of the racemates, but were obtained from the active 1 : 2-bromoammine salts by the action of liquid ammonia, in accordance with the equation : $\begin{bmatrix} Br \\ NH_3 \end{bmatrix} Co\ en_2 \Big] X_2 + NH_3 =$ $\begin{bmatrix} NH_3 \\ NH_3 \end{bmatrix} Co\ en_2 \Big] \begin{matrix} X_2 \\ Br \end{matrix}$. This reaction denotes a change from an asymmetric cobalt compound to one showing molecular asymmetry I (compare A., 1911, i, 839).

1 : 2-Bromoamminediethylenediaminecobaltic bromide was used in the first experiments, but it was found that the active 1 : 2-diammine bromide obtained was always contaminated with the inactive 1 : 6-salt. The formation of the 1 : 6-isomeride was completely prevented, however, when the bromocamphorsulphonate was used instead of the bromide Recrystallisation of the product of the action of liquid ammonia on 1 : 2-bromoamminediethylenediaminecobaltic *d*-bromocamphorsulphonate gives immediately pure d-*diamminediethylenediaminecobaltic* d-*bromocamphorsulphonate*.

The active salts show very marked dispersion of the rotation, for example, the chloride has $[a]_c \pm 15°$, $[a]_D \pm 50°$; in the three-field polarimeter the *d*-salts give a yellow middle field and orange outer fields, the colours being reversed for the *l*-salts. Their rotatory powers for the *D*-line agree approximately with those of the dinitro-salts, and are about one-third of the values obtained for the triethylenediamine salts for both the *C*- and *D*-lines.

The solubilities of the active salts are, as a rule, greater than that of the racemate. Of the bromocamphorsulphonates, the *dd*- and *ll*-salts are sparingly soluble, whilst the *dl*- and *ld*-salts are easily soluble.

The cold aqueous solutions of the active salts can be preserved indefinitely without undergoing racemisation; on boiling for some time, racemisation occurs, being accompanied by a complete decomposition of the compounds.

d-*Diamminediethylenediaminecobaltic* d-*bromocamphorsulphonate* and the corresponding *ll*-*salt* were obtained by dissolving *d*-bromoamminediethylenediaminecobaltic *d*-bromocamphorsulphonate or the corresponding *ll*-salt in liquid ammonia. After a short time the solution turns yellow, and one recrystallisation of the residue after allowing the ammonia to evaporate gives the pure salt, $[a]_D^{24} + 81°$ and $- 80°$.

The following active diamminediethylenediaminecobaltic salts, YX_3,

where $Y = [(NH_3)_2Co\ en_2]$, were obtained from the active bromo-camphorsulphonates by treatment with concentrated solutions of the appropriate acids. The *chlorides*, YCl_3, form golden-yellow prisms ; the *bromides*, YBr_3, crystallise in deep-yellow needles ; the *perchlorates*, $Y(ClO_4)_3$, form yellow, prismatic crystals, and the *nitrates*, $Y(NO_3)_3$, give slender, golden-yellow, flat crystals. The *iodides*, YI_3, dark yellow crystals, and the *dithionates*, $Y(S_2O_6)_3,3\cdot5H_2O$, small, cubical crystals, are obtained from the bromides by double decomposition with ammonium iodide and sodium dithionate respectively ; the nitrate can similarly be obtained, using silver nitrate.

The specific and molecular rotations of the various salts are shown in the following table :

	$[\alpha]_D.$	$[M]_D.$	$[\alpha]_C.$	$[M]_C.$	Temp.
d-Chloride.........	$+50°$	$+159\cdot8°$	$+15°$	$+47\cdot94°$	$21\cdot0°$
l-Chloride	-51	$-162\cdot99$	-16	$-51\cdot14$	$22\cdot0$
d-Bromide..	$+87$	$+164\cdot0$	$+11$	$+48\cdot75$	$23\cdot0$
l-Bromide	-37	$-164\cdot0$	-9	$-39\cdot89$	$22\cdot0$
d-Iodide......... ...	$+29$	$+172\cdot3$	—	—	$24\cdot0$
l-Iodide	-28	$-166\cdot22$	—	—	$24\cdot0$
d-Nitrate	$+46$	$+183\cdot7$	$+14$	$+55\cdot89$	$21\cdot5$
l-Nitrate	-44	$-175\cdot65$	-12	$-47\cdot90$	$23\cdot5$
d-Perchlorate ...	$+82$	$+163\cdot7$	—	—	$22\cdot0$
l-Perchlorate ...	-83	$-168\cdot83$	-7	$-85\cdot81$	$22\cdot0$
d-Dithionate.....	$+24$	$+116\cdot86$	—	—	$23\cdot0$

T. S. P.

The Asymmetric Cobalt Atom. VIII. ALFRED WERNER and G. TSCHERNOV (*Ber.*, 1912, **45**, 3294—3301).—Optically active 1:2-chloro-bromodiethylenediaminecobaltic salts, $\left[\begin{matrix}Cl\\Br\end{matrix}Co\ en_2\right]X$, are described.

The inactive 1:2-chlorobromo-bromide, which was used as the starting point, was obtained as follows : 1:6-dichlorodiethylenediaminecobaltic chloride (compare A., 1912, i, 82) was prepared, and transformed into 1:2-chloroaquodiethylenediaminecobaltic sulphate. From the latter, chloroaquodiethylenediaminecobaltic bromide was obtained and transformed, by heating at 105°, into a mixture of the 1:2- and 1:6-chloro-bromodiethylenediaminecobaltic bromide, from which the 1:2-isomeride is obtained by means of its lesser solubility (compare A., 1912, i, 83).

The active chlorobromo-salts were obtained by treating an aqueous solution of the racemic bromide with active ammonium bromocamphor-sulphonate (compare the preparation of the active dichloro-salts, A., 1912, i, 11). After a short time, when ammonium *d*-bromo-camphorsulphonate is used, a microcrystalline precipitate of *l*-chloro-bromodiethylenediaminecobaltic *d*-bromocamphorsulphonate separates, whereas ammonium *l*-bromocamphorsulphonate gives the *dl*-salt. The salts are very unstable in aqueous solution, readily giving the bromo-aquo-salts, so that all operations must be carried out as quickly as possible.

The various active salts were obtained from the bromocamphor-sulphonates by trituration with the requisite concentrated mineral acid until complete solution was attained ; the strongly-cooled solutions were then precipitated with alcohol.

The following table (rows 1 and 2) gives a summary of the rotatory powers of the various salts ; for the sake of comparison, the rotations of the dichloro-salts are also given (rows 3 and 4) :

	Chloride.		Bromide.		Nitrate.		Sulphate.		Dithionate.	
	$[a]$.	$[M]$.	$[a]$.	$[M]$.	$[a]$.	$[M]$.	$[a]$.	$[M]/2$.	$[a]$.	$[M]/2$.
d-Salt...	$+164°$	$+571°$	$+148°$	$+531°$	$+144°$	$+513°$	$+144°$	$+506°$	$+116°$	$+445°$
l-Salt..	-176	-612	-155	-608	-152	-542	$-148°$	-520	-120	-460
d-Salt...	$+184$	$+558$	$+168$	$+554$	$+164$	$+511$	$+180$	$+536$	$+160$	$+542$
l-Salt...	-200	-607	-176	-581	-164	-511	-182	$-540·5$	-164	-556

The above are the maximum values observed, since racemisation takes place very rapidly.

l-*Chlorobromodiethylenediaminecobaltic* d-*bromocamphorsulphonate*,

$$Y(SO_3 \cdot C_{10}H_{14}OBr),$$

where $Y = \begin{bmatrix} Cl \\ Br \end{bmatrix} Co\ en_2$, forms a grey, crystalline powder with a violet shade ; $[a]^{20} - 40°$, $[M]^{20} - 242°$. The corresponding ' dl-*salt* is similar ; $[a]^{20} + 32°$, $[M]^{20} + 193°$. The active *chlorobromodiethylenediaminecobaltic chlorides*, YCl,H_2O, are dark, greyish-violet, crystalline powders, as also are the *bromides*, YBr,H_2O, and the *nitrates*, YNO_3. The *sulphates*, Y_2SO_4,H_2O, and *dithionates*, $Y_2S_2O_6,H_2O$, are respectively light violet, crystalline powders and light grey leaflets. T. S. P.

a-Aminobutyric Acid and its Derivatives. EMIL ABDERHALDEN and ERICH WURM (*Zeitsch. physiol. Chem.*, 1912, **82**, 167—171. Compare Abderhalden and Chang, A., 1912, i, 338).—When pure a-aminobutyric acid is treated with concentrated hydrochloric acid under the conditions prevailing during protein hydrolysis, only about 5% of the acid undergoes decomposition. Alanine and leucine remain unchanged under these conditions.

The conditions for the preparation of pure formyl-*d*- and -*l*-aminobutyric acid are described. Formyl-*d*-aminobutyric acid has $[a]_D^{20} - 27·74°$, the value for the isomeride being $+27·98°$.

The formyl group is readily hydrolysed by water.

On feeding *dl*-aminobutyric acid or glycyl-*dl*-aminobutyric acid to rabbits, neither the acids nor their components could be detected in the urine. E. F. A.

Preparation of Creatine from Urine. ALOIS VIQUERAT (D.R.-P. 251937).—A modification of Neubauer's method (compare Abderhalden, *Lehrbuch Biochem. Arbeitsmethoden*, 1910, III, 783) by which creatine is isolated from urine as its zinc chloride double salt. F. M. G. M.

Some Complex Compounds of Platinous Chloride with Aminoacetal. J. TSCHUGAEV and B. ORELKINE (*Compt. rend.*, 1912, **155**, 1021—1023).—An endeavour to prepare two isomeric substances of the type, $[Pt(NHMe_2)_2Cl_2]$, prepared by Jörgensen (A., 1906, i, 338), replacing the dimethylamine by aminoacetal. On adding aminoacetal to a dilute solution of potassium platinosochloride, a yellow, crystalline compound is deposited, crystallising from alcohol in needles,

m. p. 133°. It has the composition (Pt2ACl$_2$), where A stands for tho aminoacetal molecule, NH$_2$·CH$_2$·CH(OEt)$_2$. This substance is a very feeble electrolyte, and is almost unacted on by silver nitrate in alcoholic solution. In benzene solution it polymerises as shown by cryoscopic molecular weight determinations. The mother liquors from its preparation on evaporation yield a colourless, crystalline *compound*, (Pt4A)Cl$_2$, m. p. 130 5°, the chlorine of which is immediately precipitated by silver nitrate. With potassium platinosochloride it yields a *salt*, (Pt4A)PtCl$_4$, pink needles, m. p. 127°, which is not acted on by Reiset's chloride I.

An attempt was made to prepare the two isomerides having the constitution (Pt2A2NH$_3$)Cl$_2$, but it only yielded gummy products which with potassium platinosochloride gave the same *salt*,

$$(\text{Pt2A2NH}_3)\text{PtCl}_4,$$

lilac needles, m. p. 151°. W. G.

The Nitrile and Sulphonamide of Thiodiacetic Acid. NILS VON ZWEIGBERGK (*Ber.*, 1912, **45**, 3337—3338).—Dry hydrogen sulphide and ammonia are led into an ethereal solution of chloroacetonitrile until the solution, which first becomes warm, begins to cool. After collecting the precipitated ammonium chloride and concentrating the filtrate, white, rhombic tablets of the *nitrile* of thiodiacetic acid, S(CH$_2$·CN)$_2$, are obtained, m. p. 45·5—46·5°. Acetone may be used instead of ether as solvent. The substance cannot be obtained by the action of phosphoric oxide on ammonium thiodiacetate.

If, instead of proceeding as above, an ammoniacal, alcoholic solution of chloroacetonitrile is saturated with hydrogen sulphide, yellowish-white leaflets of the *sulphonamide* of thiodiacetic acid, S(CH$_2$·CS·NH$_2$)$_2$, m. p. 124—125°, are obtained. T. S. P.

Constitution of the Compound known as Phorononitrile, and on Some Other Derivatives of Phoronic and Mesitylic Acids. J. MILIKAN (*Rec. trav. chim.*, 1912, **31**, 287—298).—The true nitrile of phoronic acid should have the formula C$_{11}$H$_{16}$ON$_2$, whereas the so-called nitrile discovered by Pinner (A., 1881, 790) has the formula C$_{11}$H$_{18}$O$_2$N$_2$. Applying the conclusions drawn by Anschütz in the case of mesitonic acid (A., 1888, 1272) to the present question, the relation of these nitriles to phorone should be represented thus : Phorone, CMe$_2$:CH·CO·CH:CMe$_2$. Nitrile, CN·CMe$_2$·CH$_2$·CO·CH$_2$·CMe$_2$·CN. Amide,

$$\text{NH}_2\text{·CO·CMe}_2\text{·CH}_2\text{·CO·CH}_2\text{·CMe}_2\text{·CO·NH}_2.$$
$$\text{CMe}_2\text{·CH}_2\text{·C·CH}_2\text{·CMe}_2.$$

So-called nitrile,

$$\text{CO——NH NH-CO}$$
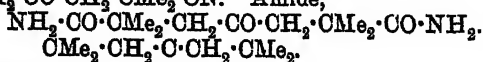
As the direct addition of hydrogen cyanide to such an unsaturated ketone as phorone would be extremely difficult, an attempt has been made to prepare the amide. *Methyl phoronate*, C$_{13}$H$_{22}$O$_5$, obtained in white needles, m. p. 30°, by the action of methyl alcohol and sulphuric acid on phoronic acid, was heated for some hours with alcoholic ammonia in a sealed tube, when, instead of the expected amide, the so-called phorononitrile was the product, m. p. 326—327°.

As the amide group is in the favourable γ position with respect to the ketone group, it is assumed that the expected amide has lost water and that the phorononitrile is a di-lactam or an anhydrodiamide of the above constitution. It is possible to replace the hydrogen attached to the nitrogen in compounds of this structure, and, in fact, *diacetylanhydrophoronodiamide*, $C_{15}H_{22}O_4N_2$, m. p. 89—90°, has been obtained by the action of acetic anhydride. The compound is also very stable and dissolves in cold concentrated nitric acid, yielding a crystalline mass which is probably an additive product with the acid, and from which, water recovers the material unchanged.

Analogous anhydrodiamides are the imidopimelimide of Marckwald (A., 1888, 677; compare also Volhard, A., 1892, 433) and the ketodi-imide of β-acetylglutaric acid of Emery (A., 1897, i, 325).

Pinner's phoronimide (*loc. cit.*) also yields the anhydrodiamide on heating with ammonia, and, accepting Anschütz's di-lactone structure for the parent substance phoronic anhydride, it is probable that the imide is a lactone-anhydroamide of the constitution

$$CMe_2 \cdot CH_2 \cdot C \cdot CH_2 - CMe_2$$

$$CO - NH \; O - CO.$$
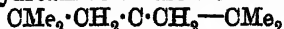
Methyl phoronate and the di-lactone have also been heated with methylamine, the product being *anhydrophoronodimethyldiamide*, $C_{13}H_{22}O_2N_2$, m. p. 136—137°, which is much less stable than the unsubstituted anhydrodiamide, since it readily loses methylamine on warming with potassium hydroxide. The *product* of the action of methylamine on the di-lactone in the cold has the formula $C_{13}H_{26}O_4N_2$ and m. p. 116—118°, and from analogy to the fact that ammonia forms with hydrochelidonodi-lactone (Volhard, *loc. cit.*) and with β-acetylglutarodilactone (Emery, *loc. cit.*) ammonium salts of amino-acids, it probably has the constitution

$$CMe_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CMe_2$$
$$OC \cdot NHMe \qquad OC \cdot OH, NH_2Me.$$
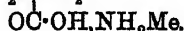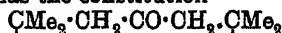
It decomposes at its melting point, and the *product*, $C_{12}H_{19}O_3N$, m. p. 110°, is, most likely, the lactone of anhydrophoronomethylamide,

$$CMe_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CMe_2$$

$$OC - NMe \; O - CO.$$
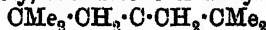
Methyl mesitylate, $C_9H_{15}O_3N$, has also been prepared in colourless needles, m. p. 119—120°.   J. C. W.

The Formation of Metallic Nitrides from Thiocyanates and Cyanides. ALEXANDER C. VOURNASOS (*Zeitsch. anorg. Chem.*, 1912, 77, 191—196. Compare A., 1911, ii, 600).—Aluminium, in the form of an impalpable powder, reduces many organic nitrogen compounds, with formation of the nitride; thus, with thiocarbamide, the reaction is $CS(NH_2)_2 + 2Al = Al_2N_2 + H_2S + H_2 + C$.

Potassium and ammonium thiocyanates, dried and mixed with aluminium powder, react if placed in a covered crucible and heated by the blowpipe according to the equation : $2K \, CNS + 2Al = {}_2S_2 + Al_2N_2 + 2C$, but a secondary reaction occurs to some extent between

the aluminium nitride, carbon, and potassium sulphide : $2K_2S +$ $Al_2N_2 + 2C = Al_2S_3 + 2KCN + K_2S$. Washing the product with alcohol gives a residue consisting of aluminium and carbon. Boron reacts in a similar manner.

Magnesium reacts violently with thiocyanates, more quietly with cyanides : $2KCN + 3Mg = Mg_3N_2 + 2K + 2C$, the product containing free potassium, whilst some carbide is formed at higher temperatures.

Glucinum reacts quantitatively with cyanides : $3Gl + Hg(CN)_2 =$ $Gl_3N_2 + Hg + 2C$, and calcium reacts in a similar manner.   C. H. D.

The Supposed Case of Isomerism with Potassium Ferricyanide. Otto Hauser and E. Biesalski (*Ber.*, 1912, 45, 3516—3521).—The supposed green isomeride of potassium ferricyanide (compare Locke and Edwards, A., 1899, i, 407 ; Bellucci and Sabatini, A., 1911, i, 430) is simply the ordinary salt containing some Prussian-blue as impurity ; the aqueous solution contains the Prussian-blue in collodial solution. An artificial mixture of potassium ferricyanide and Prussian-blue answers to all the reactions of the supposed green isomeride, and gives the same absorption and ultramicroscopic phenomena. The non-formation of the ferri-imido-ester (compare Bellucci and Sabatini, *loc. cit.*) from the green isomeride, or at all events its formation to a limited extent, is due to the catalytic effects of the decomposition product.

The above agrees with Piutti's observation (A., 1912, ii, 712) that the red and green forms have exactly the same absorption spectrum.
                                                                T. S. P.

Complex Compounds of Iron and the Formation of Nitroprusside. Paul Schwarzkopf (*Abhandl. deut. naturwiss-med. Ver. Böhmen*, 1911, 3 ; Reprint 55 pp.) —The assumption that the formation of nitroprusside occurs accoıding to two consecutive reversible reactions :
$$K_4FeCy_6 + NaNO_2 \rightleftharpoons K_3Na(FeCy_5NO_2) + KCN \text{ and}$$
$$K_3Na(FeCy_5NO_2) + H_2O \rightleftharpoons K_2(FeCy_5NO) + KOH + NaOH$$
has been tested by titrimetric estimation of the alkali present after equilibrium is reached, and the results when substituted into an equation derived to represent the conditions of the equilibrium, yield good constants. Considering the reactions from the ionic point of view, $(FeCy_6)''' +$ $(NO_2') \rightleftharpoons (FeCy_5NO_2)'' + Cy'$ and $(FeCy_5NO_2)''' + H_2O \rightleftharpoons$ $(FeCy_5NO)'' + 2OH''$, the first stage seems to imply a dissociation of the ferrocyanide ion into $(FeCy_5)'''$ and Cy' ; this is quite probable as mercuric chloride in not too dilute solution of potassium ferrocyanide precipitates an iron ferrocyanide apparently indicative of a series of dissociations finally reaching the ferrous ion ; similarly formaldehyde which is well known to combine with hydrocyanic acid, acts on a warm solution of potassium ferrocyanide, forming a deposit consisting of a mixture of ferrous and ferric hydroxides with a complex ferrocyanide. The power of mercuric chloride to remove cyanide ions from a solution should therefore accelerate the formation of nitroprusside by withdrawing the cyanide ion produced in the first stage of the action, and experimental investigation shows that it effects a very
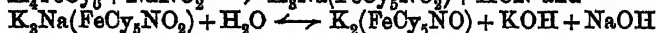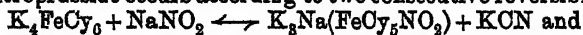
considerable acceleration. It was not found possible to prepare compounds in which more than one (CN) group of potassium ferrocyanide is replaced by (NO).

It is also discovered that nitrous acid exerts an incomplete oxidising action on an acidic solution of potassium ferrocyanide and an incomplete reducing action on acidic solutions of potassium ferricyanide ; in a similar manner it causes the oxidation of an ordinary ferrous salt and the reduction of a ferric one.   D. F. T.

Preparation and Properties of Scandium Platinocyanide. N. A. ORLOV (*Chem. Zeit.*, 1912, 36, 1407—1408).—The compounds of scandium which have hitherto been obtained leave it doubtful whether scandium must be classed with the cerium group or with the yttrium group of the rare earths.   The double sulphate with potassium sulphate resembles the double sulphates of the cerium metals, whilst the weak basic properties of scandium, and the fact that copious precipitates are obtained when the salts are boiled with solutions of sodium thiosulphate or hydrofluosilicic acid, indicates its resemblance to the yttrium metals.   The platinocyanides of the cerium metals are yellow, whilst those of the yttrium metals are red, and this should give a method of classifying scandium.   Scandium platinocyanide was obtained by concentrating the solution obtained after collecting the precipitate of barium sulphate formed on mixing equivalent solutions of scandium sulphate and barium platinocyanide.   Yellow crystals, which are very similar in appearance to cerium platinocyanide, separate from the solution, but a red, crystalline crust forms on the sides of the vessel.   On drying, the yellow crystals become reddish- or orange-coloured.   If the solution is evaporated to dryness on the water-bath a yellow residue is obtained, which becomes red on cooling.   The reverse 'change from red to yellow takes place on heating.   The yellow crystals have a composition corresponding with the formula $Sc_2(PtC_4N_4)_3,18H_2O$, whilst the red crystals have the formula
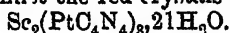
$$Sc_2(PtC_4N_4)_3,21H_2O.$$ T. S. P.

Some Metallic Salts and Complex Metallic Derivatives of Cyano-carboxylic Acids and their Esters.   LIZZIE PETTERSON (*J. pr. Chem.*, 1912, [ii], 86, 458—471).—An account of the preparation and properties of some metallic salts and derivatives of cyanoacetic and α-cyanopropionic acids.

By triturating cuprous oxide with a hot concentrated aqueous solution of cyanoacetic acid in the absence of air, a *cuprous* salt,

$$CN \cdot CH_2 \cdot CO_2Cu,3CN \cdot CH_2 \cdot CO_2H,H_2O$$
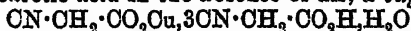
is obtained in small, white needles, which become green and melt at 119—120° when rapidly heated.

The *ferric* salt, $Fe_3(CO_2 \cdot CH_2 \cdot CN)_7(OH)_2,6H_2O$, prepared by the addition of ferric sulphate to a solution of barium cyanoacetate, forms deep, garnet-red prisms, m. p. 107° ; the *cobalt, cupric*, and *silver* salts are also mentioned.

Hydroxymercuricyanoacetic acid, $OH \cdot Hg \cdot CH(CN) \cdot CO_2H$, is obtained as a white, crystalline precipitate by shaking mercuric oxide for two days with an aqueous solution of cyanoacetic acid ; the *sodium* and

barium salts are prepared in a similar manner from the corresponding salts of cyanoacetic acid ; the *potassium* salt is prepared by the addition of potassium hydroxide to an aqueous solution of mercuric cyanide and potassium cyanoacetate.

The *methyl* and *ethyl* esters are formed by the interaction of mercuric acetate and the corresponding esters of cyanoacetic acid in methyl alcoholic solution.

Mercuric acetate reacts with ammonium cyanoacetate in aqueous solution, yielding the *compound*, $O{<}^{Hg\cdot CH(CN)\cdot CO_2}_{Hg\cdot CH(CN)\cdot CO_2}{>}Hg$, as a white, flocculent precipitate.

α-Hydroxymercuri-α-cyanopropionic acid, $OH\cdot Hg\cdot CMe(CN)\cdot CO_2H$, is a yellowish-white, crystalline substance obtained by the addition of α-cyanopropionic acid to a solution of mercuric oxide in excess of dilute acetic acid.   F. B.

The Benzene Problem. KURT GEBHARD (*J. pr. Chem.*, 1912, [ii], **86**, 540—545).—A repetition of the author's views on the structure of the benzene ring (A., 1912, ii, 242), together with a criticism of a recent paper by Liebig on this subject (A., 1912, i, 686).   F. B.

Chemical Action of Light. III. Oxidation of Benzene Hydrocarbons. HERMANN SUIDA (*Monatsh.*, 1912, **33**, 1255—1285). —The fact that the most easily isolable products of the autoxidation in light of benzene homologues are carboxy-acids is attributed to the relative instability of the intermediate products.

The most satisfactory source of light used was a quartz lamp, used at a distance of about 10 centimetres from the specimen of substance. The velocity of the first stage of the oxidation could be approximately measured by the amount of peroxide formation ; this was estimated by the action on a solution of potassium iodide acidified with dilute sulphuric acid with titration of the liberated iodine some hours afterwards. The parallel formation of carboxylic acids was estimated previously by titration with $N/30$-potassium hydroxide solution ; it appears that the amount of acid formed cannot be entirely due to the decomposition of the peroxide.

The results indicate that pure benzene is practically passive, but that the presence of thiophen causes peroxide formation. Methyl substituted benzenes undergo autoxidation when illuminated, and the action is accelerated by the presence of small quantities of nitrobenzene or of one of the nitrotoluenes. The oxidation of xylene occurs more than twice as rapidly as that of the toluenes, and *p*-xylene oxidises more rapidly than the ortho-isomeride. The oxidation of 4-nitro-*m*-xylene under the influence of light resembles that of *p*-nitrotoluene, but is feebler ; this accords with the behaviour of these substances towards chromic acid ; *p*- and *o*-nitrotoluenes are oxidisable by this reagent to the corresponding aldehydes, but 4-nitro-*m*-xylene in acetic anhydride solution containing sulphuric acid is oxidised, according to the conditions, to 4-*nitro*-m-*tolualdehyde*, small, yellow rods, m. p. 64° (*phenylhydrazone*, m. p. 108°), or the corresponding *diacetate*,

$NO_2 \cdot C_6H_3Me \cdot CH(OAc)_2$, yellow needles, m. p. 80—82°, together with some 4-nitro-m-toluic acid, m. p. 219—220°.

The results are discussed in relation to their theoretical bearing.

D. F. T.

Rational Preparation of Benzene Homologues. FRANZ KUNCKELL and GEORG ULEX (*J. pr. Chem.*, 1912, [ii], 86, 518—520. Compare Rennie, T., 1881, 41, 33).—In the preparation of the homologues of benzene by the Friedel-Craft reaction, the alkyl haloids may be replaced with advantage by the esters of chlorocarbonic acid.

When aluminium chloride is added to a mixture of the aromatic hydrocarbon and chloro-ester, several alkyl groups are simultaneously introduced, whilst if the ester is added to a cooled mixture of the hydrocarbon and aluminium chloride, the main product consists of a hydrocarbon in which only one alkyl group has been substituted.

The preparation of toluene and xylene from methyl chlorocarbonate and benzene, of trimethylbenzene from toluene, and of diethylbenzene and diethyltoluene, is described.

The *iso*butyl and amyl esters of chlorocarbonic acid give better yields than the lower homologues. F. B.

a-Phenyl-$\beta\beta$-dimethylpropane, a New Amylbenzene. ARTUR BYGDÉN (*Ber.*, 1912, 45, 3479—3483).—The interaction of magnesium benzyl chloride and *tert.*-butyl bromide in boiling ether leads to the formation of *a-phenyl-$\beta\beta$-dimethylpropane*, $CMe_3 \cdot CH_2Ph$, b. p. 185·6—186·0°, $D_4^{18\cdot5}$ 0·8581, $n_D^{18\cdot5}$ 1·48837, a colourless liquid having a pleasant, aromatic odour resembling that of anisole. C. S.

Influence of Light on the Rate of Polymerisation of Phenylbutadiene. HANS STOBBE and FRITZ REUSS (*Ber.*, 1912, 45, 3496—3498).—The formation of bisphenylbutadiene by different methods has been recorded by several investigators. The authors have performed parallel experiments, in darkness and in ordinary daylight, on phenylbutadiene in an atmosphere of carbon dioxide. The course of the polymerisation is followed by measuring the change in the refractive index It is found that the polymerisation proceeds in the dark, but is considerably accelerated by light. Assuming that the quantity of the bimolecular form is proportional to the refractive index, the unexposed hydrocarbon contains 12—13% of bisphenylbutadiene and the insolated specimen 75—76%, after two and a-half months. The polymerisation appears to be complete after seven months. C. S.

Action of Aniline on 1:3:5-Tribromo-2:4:6-tri-iodobenzene. CONSTANTIN I. ISTRATI and M. A. MIHAILESCU (*Chem. Zentr.*, 1912, ii, 1275; from *Bul. Soc. Ştiinţe Bucareşti*, 1912, 21, 23—26).—When this tribromotri-iodobenzene is heated with aniline it undergoes more extensive substitution than is the case with hexachlorobenzene (compare *ibid.*, 20, 621), and the resulting polyamines are more easily oxidised. Alcohol extracts from the product a *tribromo-iodobenzene*, needles, m. p. 154—156°, the *aniline* salt of *glyoxylic*

acid, $C_8H_{11}O_4N$, yellowish-white leaflets, m. p. 173°, and also aniline hydrobromide and iodide, whilst the amorphous, dark blue, insoluble residue has the composition of an iodopenta-anilinobenzene.

J. C. W.

Rule of the Conservation of the Type in Benzene Substitutions. ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1912, 31, 267—280).— When reviewing the introduction of further substituents into benzene rings which have already been once or twice substituted, only a few doubtful cases were found which were contrary to the rule that the position occupied is independent of the nature of the substituent. It is now shown that the bromination and the nitration of *o*-iodotoluene, the bromination of *o*-chlorotoluene, and the chlorination of *o*-chloronitrobenzene are no longer to be regarded as exceptions to the rule.

Hirtz (A., 1896, i, 531) assigned to the product obtained by brominating *o*-iodotoluene, " by analogy," the constitution

$$Me : I : Br = 1 : 2 : 4,$$
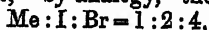
whereas Reverdin (A., 1898, i, 180) showed conclusively that the chief nitration product was $Me : I : NO_2 = 1 : 2 : 5$. The latter compound has now been reduced by means of iron powder, yielding the *iodotoluidine*, $Me : I : NH_2 = 1 : 2 : 5$, as unstable, white leaflets, m. p. 42°, which were diazotised with difficulty in hydrobromic acid solution, and converted into bromoiodotoluene, $Me : I : Br = 1 : 2 : 5$, b. p. 262—265°, $n_{14} = 1·6484$. On the other hand, the direct bromination of *o*-iodotoluene (compare Hirtz, *loc. cit.*) was accomplished in the presence of iron powder, but the product was of a very complicated nature, although the main fraction boiled at 260—265°. Direct comparison of such liquids being impossible, it was sought to obtain crystalline nitro-derivatives of them. The preparation from *o*-iodonitrotoluene, when heated with fuming nitric acid, gave 5-bromo-2 : 6-dinitrotoluene, m. p. 103°. The mixture from the direct bromination, when nitrated in acetic acid, gave a small number of yellowish-green crystals, a *bromoiododinitrotoluene*, m. p. 178—181°, which was the principal product when the highest fraction, b. p. 270—275°, was separately treated. The larger portion, however, remained in solution, and on dilution with water a product was obtained, m. p. 92—93°, which was shown to be a eutectic mixture of the above bromoiododinitrotoluene and the 5-bromo-2 : 6-dinitrotoluene. Assuming that only the 1 : 2 : 5-compound loses iodine on nitration, an estimation of the hydrogen iodide showed that this isomeride formed about 40% of the mixture. The 5-position is therefore entered to a preponderating extent by both the nitro-group and the bromine atom.

In the analogous case of the bromination of *o*-chlorotoluene it is most likely that the product is a mixture of all the possible isomerides, although it is not proved that the prevailing one is the 1 : 2 : 5. This one, however, predominates in the case of the nitration of *o*-chlorotoluene, as Wibaut will soon describe.

Cohen and Bennet (T., 1905, 87, 323) obtained by the chlorination of *o*-chloronitrobenzene the isomerides $Cl_2 : NO_2 = 1 : 4 : 2$ and $1 : 6 : 2$, and a further product which melted at 31° was said by them to be the 1 : 5 : 2 compound. The entry of chlorine into a position meta to

chlorine and para to a nitro-group is contrary to the conservation of type, and it is now shown that the doubtful product is most probably a eutectic mixture of the 1 : 4 : 2 and 1 : 6 : 2 isomerides. J. C. W.

Nitro-derivatives of 2 : 6-Dibromotoluene. JAN J. BLANKSMA (*Chem. Weekblad*, 1912, 9, 968—972. Compare A., 1912, i, 982).—A number of nitro-derivatives of 2 : 6-dibromotoluene have been prepared. The parent substance is obtained by replacing the amino-group in 6-bromo-*o*-toluidine (compare Friedländer, Bruckner, and Deutsch, A., 1912, i, 318) by bromine by the Sandmeyer method, and forms colourless crystals, m. p. 2°, and not as stated by Nevile and Winther (T., 1880, 37, 429). By the action of nitric acid (D 1·45) this substance is converted into 2 : 6-*dibromo-3-nitrotoluene*, pale yellow crystals, m. p. 50°, and not 2 : 6-dibromo-4-nitrotoluene as stated by Nevile and Winther. Its constitution was proved by its formation from 6-bromoacet-*o*-toluidide. On nitration, this substance yields 6-*bromo-3-nitroacet-o-toluidide*, yellow crystals, m. p. 199°, converted by concentrated sulphuric acid into 6-*bromo-3-nitro-o-toluidine*, orange-yellow crystals, m. p. 144°. Exchange of the amino-group of this compound for bromine by the Sandmeyer reaction yields 2 : 6-dibromo-3-nitrotoluene, identical with the product obtained by nitration of 2 : 6-dibromotoluene. Potassium permanganate does not oxidise it to the corresponding benzoic acid derivative. Further nitration converts it into 2 : 6-*dibromo-3 : 5-dinitrotoluene*, colourless crystals, m. p. 161°. Heating with alcoholic ammonia at 100° yields 6-bromo-3 : 5-dinitro-*o*-toluidine, yellow crystals, m. p. 200°; its acetyl derivative forms colourless crystals, m. p. above 300° ; at 150° the product is 3 : 5-*dinitro*-1 : 2 : 6-*tolylenediamine*, light brown crystals, m. p. 298°; the corresponding acetyl derivative forms colourless crystals, decomposing above 300°. At 150° an alcoholic solution of methylamine converts 2 : 6-dibromo-3 : 5-dinitrotoluene into 3 : 5-*dinitro*-1 : 2 : 6-*tolylenedimethyldiamine*, orange-red crystals, m. p. 216°.

Nitration of 2-bromoaceto-*p*-toluidide produces 2-*bromo-5-nitroaceto-p-toluidide*, pale yellow needles, m. p. 120°, converted by concentrated sulphuric acid into 2-*bromo-5-nitro*-p-*toluidine*, orange-red needles, m. p. 165°, which is converted by diazotisation into 2-bromo-5-nitrotoluene, identical with that obtained from 6-bromo-3-nitro-*o*-toluidine.

· Replacement of the amino-group in 2-bromo-5-nitro-*p*-toluidine by bromine by the Sandmeyer reaction yields 2 : 4-*dibromo-5-nitrotoluene*, colourless needles, m. p. 85°. Nitration with nitric and sulphuric acids converts this substance into 2 : 4-dibromo-3 : 5-dinitrotoluene, m. p. 130° (compare Davis, T., 1902, 81, 873), which with alcoholic ammonia at 150° yields 3 : 5-dinitro-1 : 2 : 4-tolylenediamine (compare A., 1904, i, 566). A. J. W.

Preparation of Anthracenemonosulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 251695).—The preparation of anthracenemonosulphonic acids has previously been

attended with difficulty; it is now found to proceed smoothly if the sulphonation is carried out in the presence of glacial acetic acid.

A solution of anthracene (300 parts) in acetic acid (600 parts) is cooled and slowly treated with chlorosulphonic acid (200 parts), the mixture is rapidly heated to 95°, and maintained at this temperature during five hours; the clear olive-green solution is treated with water (5000 parts), and the insoluble residue subsequently treated with more water (4500 parts) at 40°. The anthracene-α sulphonic acid (in 50% yield) is precipitated from the filtrate with salt, whilst the residue on treatment with a large volume of hot water furnishes anthracene-β-sulphonic acid in over 30% yield.   F. M. G. M.

Tridiphenylylmethyl.   JULIUS SCHMIDLIN (*Ber.*, 1912, 45, 3171—3183).—The tridiphenylylmethyl discovered earlier (Schlenk, Weickel, and Herzenstein, A., 1910, i, 236) is a mixture of two isomerides.

By a modification of the method of the earlier workers good yields of the tridiphenylylcarbinol could be obtained. 4-Bromodiphenyl in ethereal solution was converted by the action of magnesium and successive quantities of iodine into the corresponding organo-magnesium compound which reacted with *p*-bisdiphenylyl ketone, producing a mixture of α- and β-tridiphenylylcarbinol, together with some *p*-tridiphenylylmethane and *p*-bisdiphenyl.   p-*Tridiphenylyl-methane*, obtainable also by the reduction of the mixture of α- and β-tridiphenylylcarbinols, forms colourless crystals, m. p. 241—242° (corr.), and when recrystallised from benzene tenaciously retains benzene of crystallisation even to the m. p.; p-*bisdiphenyl* forms inodorous leaflets, m. p. 318—319° (corr.).

The isomeric carbinols, the relative proportions of which varied considerably in different experiments, could be separated by fractional recrystallisation of the mixture from ether, or by converting into a mixture of   the chlorides and then recrystallising from benzene. α-*Tridiphenylylmethylcarbinol*, the less soluble isomeride, has m. p. 212° (corr.), whilst the β-compound forms leaflets, m. p. 199—200° (corr.); both carbinols, at a concentration of 1 : 60,000, in a mixture of acetic and sulphuric acids give an absorption band from 440 to 510 μμ. The action of acetyl chloride or, better, of hydrogen chloride on the benzene solution converts the carbinols into the corresponding chlorides; α-*tridiphenylylmethyl chloride*, needles, m. p. 200° (corr.); β-*chloride*, m. p. 187—188° (corr.). The two chlorides are convertible by the action of copper powder on the benzene solution into the corresponding tridiphenylylmethyls; α-*tridiphenylylmethyl*, $C(C_6H_4Ph)_3$, is a dark green, crystalline powder, the solution of which is brownish-red, and at a concentration of 1 : 5000 shows an absorption band from 430 μμ to the ultra-violet; the molecular weight in benzene solution was 499, the theoretical being 471.

β-*Tridiphenylylmethyl* forms dark green needles, and gives a deep blue solution, which shows an absorption band (at a concentration 1 : 6000) extending from 600 to 640 μμ; the molecular weight in benzene was 518.   The two tridiphenylylmethyls easily undergo

atmospheric oxidation, producing the α- and β-*tridiphenylylmethyl peroxides*, m. p. 213° (corr.) and 198° respectively.

Experiments were made to ascertain whether so-called triphenyl-methyl can be observed to dissociate into the unimolecular condition. Gomberg and Cone (A., 1904, i, 658) obtained molecular weights in phenol solution indicating a dissociation, but this result was due to chemical interaction between solvent and solute with the formation of *p*-hydroxytetraphenylmethane, m. p. 282°, and triphenylmethane. By determining the alteration of m. p. and b. p. successively with the same benzene solution, it is now shown that the molecular weight is the same at both temperatures, and is only a little lower than that calculated for the bimolecular condition. The alteration in the colour of solutions of triphenylmethyl on warming is, therefore, probably not due to dissociation. D. F. T.

Phenyldiphenylylnaphthylmethyl. JULIUS SCHMIDLIN and ANTONIO GARCIA-BANUS (*Ber.*, 1912, **45**, 3183—3188).—The authors have succeeded in preparing triarylmethane compounds containing an asymmetric carbon atom.

p-*Diphenylyl* α-*naphthyl ketone*, $C_6H_4Ph \cdot CO \cdot C_{10}H_7$, obtained by the action of naphthoyl chloride on diphenyl in carbon disulphide solution under the influence of aluminium chloride, forms plates, m. p. 142° (corr.); when heated with aluminium chloride at 140—145°, it condenses to *phenylbenzanthrone* (annexed formula), golden-yellow plates, m. p. 178—179° (corr.), which gives a fluorescent red solution in concentrated sulphuric acid. The above diphenylyl naphthyl ketone reacts with magnesium phenyl iodide giving *phenyl-p-diphenylyl-α-naphthylcarbinol*, $C_{10}H_7 \cdot CPh(C_6H_4Ph) \cdot OH$, prisms (with ether of crystallisation), m. p. 115—116° (corr.), m. p. when ether-free 164—165° (corr.), together with a small amount of a *substance*, m. p. 197—198°, possibly phenyl-*p*-diphenylyl-α-naphthylmethane. The carbinol, which dissolves in concentrated sulphuric acid to a violet solution, reacts in benzene solution with hydrogen chloride with the formation of *phenyl-p-diphenylyl-α-naphthylmethyl chloride*, a colourless, crystalline powder, m. p. 198—199° (corr.). In an atmosphere of carbon dioxide the chloride is reduced by copper powder to *phenyl-p-diphenylyl-α-naphthylmethyl*, an apparently homogeneous product (compare preceding abstract); this dissolves in benzene to a brown solution, and from the fact that the solution, after most of its colour has been destroyed by atmospheric oxidation, recolorises to some extent, it is suggested that, unlike tridiphenylmethyl, the present substance is not completely dissociated into the active unimolecular condition; the fresh solution (concentration 1 : 5000) shows a broad absorption band from the violet end of the spectrum to 480μμ, and a small band in the yellow; the fresh solution of the corresponding phenyl-*p*-diphenylyl-α-naphthylcarbinol in sulphuric acid gives an absorption spectrum with a band extending from 480μμ half way into the green. Solutions of the above phenyl-*p*-diphenylyl-α-naphthylmethyl are

oxidised by the atmosphere to the *peroxide*, $(C_{29}H_{21})_2O_2$, a colourless, crystalline powder, m. p. 158° (corr., decomp.).

Although triphenylmethyl chloride, by the action of menthol in pyridine solution, can be converted into *triphenylmethyl l-menthyl ether*, m. p. 137—138° (corr.), similar treatment of phenyl-*p*-diphenylyl-*a*-naphthylmethyl chloride produced only the corresponding carbinol. It was also found impossible to prepare the camphorate or camphor-sulphonate. The chloride of the carbinol will not react with nicotine or coniine, and the product obtained by replacing the halogen by the amino-group is not basic in properties. The most promising method for the resolution of the asymmetric carbinol into its enantiomorphous constituents appears to depend on the active *amyl ether* which has been obtained in the crystalline state.   D. F. T.

Reduction of Aromatic Alcohols with Aliphatic Alcohols. JULIUS SCHMIDLIN and ANTONIO GARCIA-BANÙS (*Ber.*, 1912, **45**, 3188—3193 *).—By using sulphuric acid as solvent, the reduction of aromatic secondary and tertiary carbinyl chlorides by aliphatic alcohols, already observed in special cases (for example, Kauffmann and Fritz, A., 1909, i, 99), becomes a fairly general reaction. Triphenylcarbinol and triphenylmethyl chloride, in a mixture of equal volumes of alcohol and sulphuric acid, undergo reduction to triphenylmethane, the action being represented : $CPh_3 \cdot SO_4H + EtOH = CHPh_3 + CH_3 \cdot CHO + H_2SO_4$; the ethyl alcohol can be replaced by methyl alcohol. In a similar manner tridiphenylylmethane and diphenylmethane can be obtained from tridiphenylylmethyl chloride or tridiphenylylcarbinol and benzhydrol respectively. The reaction fails with the naphthalene-carbinols, and also in cases where the sulphuric acid itself can cause dehydration or other effects, as, for example, with *aβ*-diphenylethyl alcohol, which yields stilbene.

The reduction of triphenylmethyl in ethereal solution by hydrogen and platinum black produces only triphenylmethane.

The oxidation of triphenylmethane to the corresponding carbinol can be quantitatively effected by boiling nitric acid, D 1·33 (compare Schwarz, A., 1909, i, 561).

A diagram is given for an apparatus designed for the preparation of fairly large quantities of triphenylmethyl and analogous compounds.

Endeavours to prepare a "mixed" ethane derivative by the inter-action of magnesium triphenylmethyl chloride and tridiphenylylmethyl chloride produced only a mixture of triphenylmethyl and tridiphenylyl-methyl ; also no crystalline product could be obtained from the same Grignard reagent and phenylfluorenyl chloride.   D. F. T.

Valency of Carbon, Arsenic, and Silicon. WILHELM SCHLENK (*Annalen*, 1912, **394**, 178—223).—[With LEOPOLD MAIR.]—The deepening of the colour of a solution of triphenylmethyl by warming has been attributed to the shifting of the equilibrium of the system $CPh_3 \cdot CPh_3 \rightleftharpoons 2CPh_3$ from left to right. Gomberg has shown by the cryoscopic method that triphenylmethyl in cold benzene exists almost entirely as hexaphenylethane. The authors now show by the ebullio-

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* and *Anal. Fis. Quim.*, 1212, **10**, 449—454.

scopic method that at its b. p. the solution contains about 25% of triphenylmethyl.

Since triphenylmethyl peroxide and diphenylenephenylmethyl oxide (diphenylfluorene ether; Kliegl, A., 1905, i, 187) are comparatively stable substances, the authors hoped to prepare triphenylmethyl oxide, $(CPh_3)_2O$, from chlorotriphenylmethane by the action of silver oxide or of the sodium derivative of triphenylcarbinol. The products in both cases, however, are triphenylcarbinol and resinous substances.

[With C. BORNHARDT.]—The same products are also obtained by the oxidation of triphenylmethyl in glacial acetic acid or acetone by chromic acid or potassium permanganate.

After keeping triphenylmethyl and sulphur in carbon disulphide in darkness for six to eight weeks, the hydrocarbon is completely converted into an inseparable mixture of triphenylmethyl polysulphides.

A benzene solution of triphenylmethyl and an alcoholic ethereal solution of diazomethane react to form *hexaphenylpropane*,

$$CPh_3 \cdot CH_2 \cdot CPh_3,$$
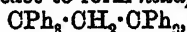
a more complete description of which is promised.

[With JULIUS RENNING.]—By heating a benzene solution of phenyl-xanthenol chloride, prepared by Gomberg's method (A., 1910, i, 56), with copper-bronze on the water-bath, *phenylxanthyl*,

$$C_6H_4 \underset{O}{\overset{CPh}{<}} C_6H_4,$$
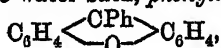
is obtained. It forms brown crystals which disintegrates to a yellow powder at 60° in carbon dioxide, and is shown to be present in the unimolecular form to the extent of about 82% in boiling 1—2% benzene solution by the ebullioscopic method. *Phenylthioxanthyl*, $C_6H_4 \underset{S}{\overset{CPh}{<}} C_6H_4$, prepared in a similar manner from phenylthio-xanthenol chloride (Gomberg, A., 1910, i, 869), is a brownish-red, crystalline powder, and is present in the unimolecular form to the extent of about 14% in cold benzene. *Phenylanthronyl*,

$$C_6H_4 \underset{CO}{\overset{CPh}{<}} C_6H_4,$$
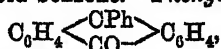
is a yellow, crystalline powder; a 1—2% benzene solution contains in the cold about 33% of the unimolecular form. *Diphenyl-a-naphthyl-methyl*, $C_{10}H_7 \cdot CPh_2$, obtained by boiling *chlorodiphenyl-a-naphthyl-methane*, m. p. 163°, with copper bronze in petroleum, b. p. 60—75°, in an atmosphere of carbon dioxide, is a greyish-black powder; a 2—3% solution in cold benzene contains about 59% of the uni-molecular form. *Phenyl-p-diphenylyl-a-naphthylmethyl*,

$$C_6H_4Ph \cdot CPh \cdot C_{10}H_7,$$
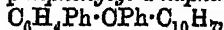
prepared in a similar manner from *chlorophenyldiphenylyl-a-naphthyl-methane*, m. p. 194·5°, is an olive-brown powder; a 1—3% solution in cold benzene contains the unimolecular form almost entirely.

[With LEOPOLD MAIR.]—p-*Anisyldiphenylenecarbinyl chloride*,

$$\overset{C_6H_4}{\underset{C_6H_4}{>}} CCl \cdot C_6H_4 \cdot OMe,$$
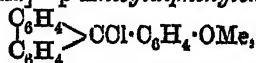
m. p. 149—151°, prepared by treating fluorenone with magnesium p-anisyl iodide in ether, decomposing the product in the usual manner,

and saturating a cold ethereal solution of the resulting carbinol with hydrogen chloride, reacts with copper-bronze in boiling benzene in an atmosphere of carbon dioxide to form *di-p-anisylbisdiphenylene-ethane*, $C_{40}H_{30}O_2$, m. p. 170—190° (decomp.) in open tube, 227—230° in carbon dioxide in a closed tube.   It is a white, crystalline powder, stable in air, and forms solutions which become brown by warming and almost colourless again by cooling ; its solution in benzene absorbs oxygen and yields the *peroxide*, $C_{40}H_{30}O_4$, m. p. 192°, colourless prisms.

[With ANNA HERZENSTEIN.]—The formation of triarylmethyls by the action of metals on solutions of triarylcarbinyl chlorides bears some resemblance to the elimination by one metal of another from a solution of its salts.   In fact, when equal molecular quantities of triphenylmethyl and of phenyldidiphenylylcarbinyl chloride are brought together in benzene, the colour of the solution quickly darkens in consequence of the liberation of red phenyldidiphenylylmethyl by the yellow triphenylmethyl.   Still more striking is the reaction which occurs when a benzene solution of phenylnaphthyldiphenylylcarbinyl chloride is added slowly to a solution of triphenylmethyl ; each drop produces, with the rapidity of an ionic reaction, the deep reddish-brown coloration of phenyldiphenylylnaphthylmethyl.

[With GEORG RACKY and C. BORNHARDT.]—Attempts to prepare tervalent carbon derivatives containing radicles other than aryl groups show that such substances are not formed or usually exist in the dimolecular state ; thus Wieland's benzpinacone diphenyl ether exists as such ; only at high temperatures does it change to phenoxy-diphenylmethyl (A., 1911, i, 851).   The action of metals on chlorides of the type CAr_2RCl should yield hydrocarbons CAr_2R.   When R is methyl or other alkyl group containing CH, however, the chloride cannot be isolated, since it spontaneously loses hydrogen chloride with the formation of diarylolefines.   *Diphenyl-tert.-butylcarbinyl chloride*, $CPh_2Cl\cdot CMe_3$, m. p. 103—106°, large, colourless crystals, can be obtained by the interaction of magnesium phenyl bromide and ethyl trimethylacetate in ether, the product, isolated in the usual manner being saturated in ether with hydrogen chloride and finally boiled with acetyl chloride.   By boiling in xylene with sodium, the chloride yields *diphenyldi-tert.-butylethane*, $CMe_3\cdot CPh_2\cdot CPh_2\cdot CMe_3$, which has no tendency to dissociate into the tervalent carbon derivative. *βββ-Trichloro-α-bromo-αα-diphenylethane*, $CPh_2Br\cdot CCl_3$, m. p. 87·5°, colourless crystals, obtained by treating the trichlorodiphenylethane with an excess of bromine, loses chlorine and bromine by treatment with metals.

By treatment with liquid nitrogen peroxide, tetraphenylethylene in chloroform yields *pp'-dinitrotetraphenylethylene*,

$$NO_2\cdot C_6H_4\cdot CPh\colon CPh\cdot C_6H_4\cdot NO_2,$$
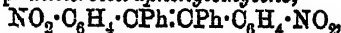
m. p. 150—190°, citron-yellow crystals.   In boiling nitrobenzene the two substances do not react.   Bis-diphenylene-ethylene in chloroform and nitrogen peroxide yield *dinitrobisdiphenylene-ethane*,

$$\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}{>}C(NO_2)\cdot C(NO_2){<}\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix},$$
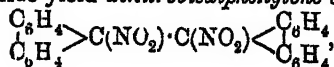
colourless crystals, which is stable, but decomposes by melting (178°) and yields fluorenone and nitric oxide, whilst by heating with phenol it yields nitrophenol and bisdiphenylene-ethylene.

Tetradiphenylylethylene, which is obtained readily by boiling *diphenylyl ketochloride*, $CCl_2(C_6H_4Ph)_2$. m. p. 136°, in xylene with copper bronze, reacts with nitrogen peroxide in chloroform to form a blue substance, which rapidly decomposes, yielding diphenylyl ketone.

[With GEORG RACKY.]—The vapour density of arsenic disulphide at about 900° corresponds with the formula As_2S_3. The authors' experiments on the molecular weight of arsenic di-iodide in boiling benzene lead conclusively to the formula As_2I_4 (compare Hewitt and Winmill, T., 1907, 91, 962). The molecular weight of tetraphenyl-cacodyl in boiling benzene corresponds with the formula As_2Ph_4. Consequently there is no evidence of the existence of bivalent arsenic compounds.

[With JULIUS RENNING.]—Silicon tetrachloride in ether is treated with magnesium phenyl bromide (2 mols.) and subsequently with magnesium methyl iodide. After treatment with water, the mixture is fractionally distilled, whereby *diphenylsilicoethylene*, $SiPh_2:CH_2$, is obtained. It is a colourless, odourless liquid, b. p. 266—268°/720 mm., which does not react with bromine or decolorise alkaline potassium permanganate.   C. S.

Spirans. VI. Some Properties of the Spiran Carbon Atom. DAN RADULESCU (*Chem. Zentr.*, 1912, ii, 1363—1366; from *Bul. Soc. Ştiinţe Bucareşti*, 21, 32—58. Compare A., 1912, i, 179).— The influence of the spiran carbon atom on the stability of, and on the conditions for the formation of, the two rings which it connects, and also on the reactivity of single members of the rings, is discussed. No steric hindrance exists which prevents the closing of spiran rings; in fact, spirans with five or six atoms in the ring are more stable than analogous compounds with open chains, so that the tendency is to form closed rings. The behaviour of the spiran carbon atom in strained ring systems has been studied in the case of *cyclo*propane-*cyclo*pentane-2 : 5-dione-1 : 1-spiran-3 : 4-dicarboxylic acid and its derivatives. The stability of the trimethylene ring is scarcely lessened by the spiran carbon atom.

The chromophoric properties of the rings are also affected by the quaternary system of the spiran carbon atom ; the two spiran bonds in one ring act like a double link on the other ring. The group II is a stronger chromophore than the group I.

(I.)   (II.)   (III.)
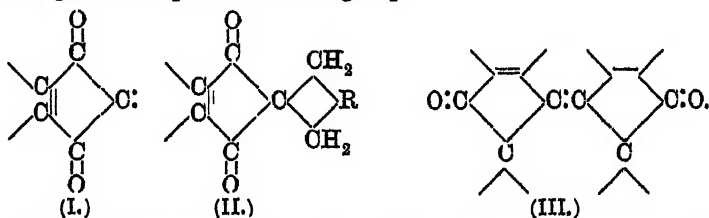
Anhydro-derivatives of the type III give yellow solutions which

with strong alkalis become blue. Carminic acid develops the same colour with very concentrated, strong bases, and has an absorption spectrum which is almost identical with that of compounds of this type.

Fecht's indan-1 : 3-dione-indan-2 : 2-spiran (xylylenediketohydrindene) (A., 1907, i, 906) is found to be impure. Repeated solution in benzene and precipitation with light petroleum separates from it *anhydrobis-indan*-1 : 3-*dioneindan*-2 : 2-*spiran*, $C_{34}H_{22}O_3$, (V), in pale yellow flakes, m. p. 256—257°, which give with phenylhydrazine the brownish-red hydrazone of Fecht's spiran. A very dilute alcoholic solution develops an intense indigo colour with a drop of concentrated potassium hydroxide, whereas the pure indan-1 : 3-dione-indan-2 : 2-spiran (IV) gives no coloration. The latter forms golden-yellow, thick prisms, m. p. 149°, and gives a violet colour to concentrated sulphuric acid. The ethereal mother liquors from this compound still contain *indan*-1 : 3-*dione*-1-*ethoxyindan*-2 : 2-*spiran*, $C_{19}H_{16}O_3$, (VI), which forms yellow prisms, m. p. 199—200°, and imparts a red colour to sulphuric acid, but is not affected by alkalis.

$$(IV.) \quad C_6H_4 \underset{CO}{\overset{CO}{\diamondsuit}} C \underset{CH_2}{\overset{CH_2}{\diamondsuit}} C_6H_4$$

$$(VI.) \quad C_6H_4 \underset{CO}{\overset{CO}{\diamondsuit}} C \underset{CH \cdot OEt}{\overset{CH_2}{\diamondsuit}} C_6H_4$$

$$(V.) \quad C_6H_4 \underset{\overset{C}{C}}{\overset{CO}{\diamondsuit}} C \underset{CH_2}{\overset{CH_2}{\diamondsuit}} C_6H_4 \quad ; \quad C_6H_4 \underset{CH_2}{\overset{C}{\diamondsuit}} C \underset{CO}{\overset{CH_2}{\diamondsuit}} C_6H_4$$
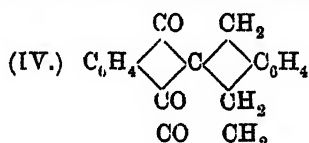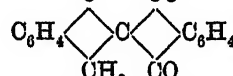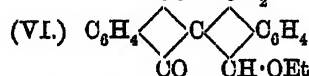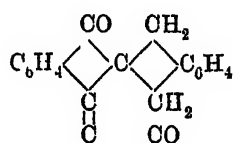
1-*Imino*-3-*indanoneindan*-2 : 2-*spiran*, $C_{17}H_{13}ON$, (VII), obtained by heating the spiran (IV) with alcoholic ammonia, separates in brick-red flakes.

$$(VII.) \quad C_6H_4 \underset{C:NH}{\overset{CO}{\diamondsuit}} C \underset{CH_2}{\overset{CH_2}{\diamondsuit}} C_6H_4$$

$$(VIII.) \quad \overset{CH_2}{\underset{CH_2}{>}} C \overset{CO}{\underset{CO}{<}} \overset{CH \cdot CO_2H}{\underset{CH \cdot CO_2H}{}}$$
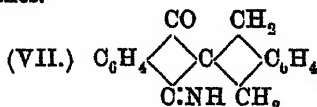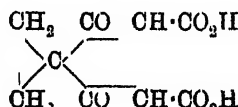
*cyclo*Propane*cyclopentanedione*-1 : 1-*spiran*-3 : 4-*dicarboxylic acid*, (VIII), from ethyl *cyclo*propane-1 : 1-dicarboxylate, ethyl succinate, and sodamide, is converted at 180—200° or by heating with acetic anhydride into the *anhydride*, $C_9H_6O_5$, small, white needles.

Bisdihydroxyquinoline - 3 : 3 - *spiran* (*bisdihydrocarbostyrylspiran*), $C_{17}H_{14}O_2N_2$, (IX), from the reduction of ethyl di-*o*-nitrobenzyl-malonate, sublimes above 360° in colourless, shining flakes, which dissolve when hydrogen bromide is passed into a suspension of the substance in acetic acid.

$$(IX.) \quad C_6H_4 \underset{N \quad C}{\overset{CH_2}{<}} C \overset{CH}{\underset{C \quad N}{>}} C_6H_4$$
$$\overset{}{\underset{OH \quad OH}{}}$$

$$(X.) \quad C_6H_4 - H_2C - C - CH_2 - C_6H \quad$$
$$\overset{}{\underset{NH_2 \quad EtO_2C \quad CO_2Et \quad NH_2}{}}$$
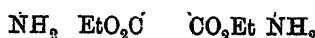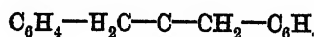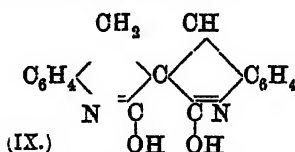
When the mother liquors from the reduction are treated with

ammonia, the reddish primary product of the reaction, the *amino*-ester (X), separates out. It readily loses alcohol, forming the spiran.

Ethyl di-p-nitrobenzylmalonate, $C(CH_2 \cdot C_6H_4 \cdot NO_2)_2(CO_2Et)_2$, white needles, m. p. 171°, is the chief product when ethyl dibenzylmalonate is nitrated by fuming nitric acid in glacial acetic acid.

J. C. W.

Stereochemistry of Quinquevalent Nitrogen. I. Formation and Decomposition of the Quaternary Ammonium Bases and Salts. SHIGERU KOMATSU (*Mem. Coll. Sci. and Eng., Kyoto Imp. Univ.*, 1912, **3**, 371—426).—The author has prepared a long series of quaternary ammonium compounds, and finds m. p.'s for the iodides which generally show considerable divergence from those previously stated by Jones and by Wedekind. In the thermal decomposition of the hydroxides it is observed that in the series $HO \cdot NPh(CH_2Ph)XY$ the benzyl group is always the one to be eliminated; with the series $HO \cdot NPh(C_3H_5)XY$, if X and Y are smaller groups than the allyl, the last undergoes scission, but if one is larger and the other smaller than the allyl, the smaller of X and Y becomes removed. Apart from these two classes it is found that, as a general rule, the smallest group is always left attached to the nitrogen atom.

The following tertiary bases and derivatives were obtained. Dimethylaniline gives a *picrate*, needles, m. p. 154—155°, and combines with mercuric chloride giving a yellow *compound*, crystallising in needles, also a basic *compound*, $O(Hg \cdot NMe_2PhCl)_2$, pearly scales, and a *double* salt, $NMe_2Ph, HCl, HgCl_2$, colourless needles. Methylethylaniline gives a *picrate*, prisms, m. p. 121—122°; *ferrocyanide*, colourless crystals, and combines with mercuric chloride producing a colourless, scaly basic *compound*, $O(Hg \cdot N \cdot PhMeEtCl)_2$, and a *double* salt, colourless needles. Methylallylaniline forms a picrate, m. p. 81—82°, and *ferrocyanide*, colourless crystals. Methylpropylaniline gives a *picrate*, m. p. 103—104°; *ferrocyanide*, colourless. Methyl-*n*-butylaniline, b. p. 225—230°, forms a *picrate*, rhombic needles, m. p. 141—142°; *ferrocyanide*, light green, crystalline powder. Methyl*iso*butylaniline yields a *picrate*, plates, m. p. 99—100°, and *ferrocyanide*, colourless. Methyl*iso*amylaniline forms a *picrate*, m. p. 93—94°, and *ferrocyanide*, light green. Benzylmethylaniline gives a *picrate*, rhombic prisms, m. p. 101—101·5°; *ferrocyanide*, colourless; colourless *double* salt, $(NMePh \cdot CH_2Ph, HCl)_2CdCl_2$, with cadmium chloride, and with mercuric chloride a mixture of a yellow *substance* (which on exposure to air is slowly converted into a blue *substance*, m. p. about 160°), a basic *substance*, crystallising in white needles (composition analogous to that of the basic substances above), and a *double* salt, $(NMePh \cdot CH_2Ph, HCl)_2, HgCl_2$, colourless needles. Ethylallylaniline gives a *picrate*, prisms, m. p. 98—99°, and *ferrocyanide*, colourless. Ethyl-*n*-propylaniline forms a *picrate*, crystalline powder, m. p. 94—95°, and *ferrocyanide*, colourless. Ethyl-*n*-butylaniline gives a *picrate*, rhombic prisms, m. p. 89—90°, and *ferrocyanide*, colourless. Ethyl*iso*butylaniline yields a *picrate*, crystals, m. p. 91—92°, and *ferrocyanide*, light green, crystalline powder. Ethyl*iso*amylaniline forms a *picrate*, rhombic prisms, m. p. 103—104°, and

ferrocyanide, light green, crystalline powder.   Benzylethylaniline gives a picrate, rhombic prisms, m. p. 110—111°; *ferrocyanide*, light green, crystalline powder, a *double* salt (colourless needles) with cadmium chloride, and with mercuric chloride a colourless, crystalline basic *substance* and a *double* salt (needles), $(NEtPh \cdot CH_2Ph, HCl)_2, HgCl_2$. Diethylaniline, *picrate*, m. p. 135—136°.

The m. p. of each of the above picrates, as also of most of the iodides below, was also determined by the Kuhara-Chikashigé method (A., 1900, ii, 260), the results differing occasionally by several degrees from those obtained by the ordinary method.

The following quaternary compounds were examined : Phenylbenzyldimethylammonium iodide, m. p. 141—142° (compare Jones, T., 1903, 83, 1409), obtained from dimethylaniline and benzyl iodide ; *platinichloride*, needles, m. p. 164—165° ; the *hydroxide* when heated decomposes, giving dimethylaniline. Phenylbenzylmethylethylammonium iodide, m. p. 135—136° (compare Jones, T., 1904, 85, 224 ; Fröhlich, A., 1910, i, 375), from methylethylaniline and benzyl iodide ; *platinichloride*, needles, m. p. 160·5—161° ; the *hydroxide* decomposes, giving methylethylaniline. Phenylbenzylmethylallylammonium iodide, rhombic prisms, m. p. 128—129° (compare Jones, T., 1905, 87, 1721 ; Wedekind, A., 1899, i, 351), obtained from methylallylaniline and benzyl iodide, or from benzylmethylaniline and allyl iodide ; *platinichloride*, needles, m. p. 133—134° ; the *hydroxide* when decomposed yields methylallylaniline.   Phenylbenzylethyl-*n*-propylammonium   iodide, prisms, m. p. 143°, from methyl-*n*-propylaniline and benzyl iodide ; *platinichloride*, needles, m. p. 159—160° ; the *hydroxide* on decomposition gives methyl-*n*-propylaniline. Phenylbenzylmethyl*iso*butylammonium iodide, prisms, m. p. 124—125°, obtained from methyl*iso*butylaniline and benzyl iodide ; *platinichloride*, needles, m. p. 147—148° ; the *hydroxide* on decomposition gives methyl*iso*butylaniline. *Phenylbenzylmethyl-n-butylammonium iodide*, needles, m. p. 132—133°, obtained from methyl-*n*-butylaniline and benzyl iodide ; *platinichloride*, needles, m. p. 139—140° ; the *hydroxide* on decomposition gives methyl-*n*-butylaniline. Phenylbenzylmethyl*iso*amylammonium iodide, from methyl*iso*amylaniline and benzyl iodide, needles, m. p. 137—138° (compare Thomas and Jones, T., 1906, 89, 280) ; *platinichloride*, needles, m. p. 149—150° ; the *hydroxide* on decomposition gives methyl*iso*amylaniline. Phenyldibenzylmethylammonium iodide, m. p. 105—106° from benzylmethylaniline and benzyl iodide (compare Jones, T., 1903, 83, 1410) ; *platinichloride*, needles, m. p. 131—132° ; the *hydroxide* on decomposition yields benzylmethylaniline. *Phenylbenzylethyl-n-propylammonium iodide* from ethyl-*n*-propylaniline and benzyl iodide, prisms, m. p. 105—106° ; *platinichloride*, needles, m. p. 146—147° ; the *hydroxide* on decomposition yields ethyl-*n*-propylaniline.

Phenylbenzylethylallylammonium iodide, obtained from ethylallylaniline and benzyl iodide, prisms, m. p. 106·5° ; *platinichloride*, needles, m. p. 138—139°.   Phenyldimethylallylammonium iodide, from dimethylaniline and allyl iodide, prisms, m. p. 84—85° ; the *hydroxide* on decomposition gives dimethylaniline. *Phenyldiethylallylammonium*

iodide from ethylallylaniline and ethyl iodide, or from diethylaniline and allyl iodide; *platinichloride*, needles, m. p. 158—159°; the *hydroxide* on decomposition gives diethylaniline. Phenylmethyl-*n*-propylallylammonium iodide, prisms, m. p. 119—120°, from methyl-*n* propylaniline and allyl iodide, or as a gummy mass from methylallylaniline and *n*-propyl iodide; *platinichloride*, needles, m. p. 157—158°; the *hydroxide* on decomposition gives *n*-propylallylaniline. Phenylmethyl*iso*butylallylammonium iodide from methyl*iso*butylaniline and allyl iodide, needles, m. p. 124°; *platinichloride*, needles, m. p. 156—157°; the *hydroxide* on decomposition yields *iso*butylallylaniline. Phenylmethyl*iso*amylallylammonium iodide, prisms, m. p. 126—127°, from methyl*iso*amylaniline and allyl iodide; *platinichloride*, needles, m. p. 154—155°; the hydroxide on decomposition gives *iso*amylallylaniline.

Phenylmethylethyl-n-butylammonium iodide, prisms, m. p. 72—73°, obtained from methylethylaniline and *n*-butyl iodide, also from ethyl-*n*-butylaniline and methyl iodide; *platinichloride*, needles, m. p. 195—196°, was obtained also from the gummy reaction product of methyl-*n*-butylaniline and ethyl iodide; the *hydroxide* on decomposition gives methyl-*n*-butylaniline. *Phenylmethylethylisoamylammonium iodide*, needles, m. p. 154°, was obtained from ethyl*iso*amylaniline and methyl iodide, also from methylethylaniline and *iso*amyl iodide, and from methyl*iso*amylaniline and ethyl iodide; *platinichloride*, m. p. 191—192°; the *hydroxide* on decomposition gives methyl*iso*amylaniline.

Phenylmethyl-n-propylisobutylammonium iodide, a viscous mass, from methyl*iso*butylaniline and *n*-propyl iodide, and also from methyl-*n*-propylaniline and *iso*butyl iodide; *platinichloride*, needles, m. p. 200—201°; the *hydroxide* on decomposition yields methyl-*n*-propylaniline.

Phenylmethyl-n-propylisoamylammonium iodide, obtained as a gummy mass from methyl*iso*amylaniline and *n*-propyl iodide and also from methylpropylaniline and *iso*amyl iodide; platinichloride, needles, m. p. 183—183·5°; the hydroxide on decomposition gives methyl-*n*-propylaniline. *Phenylmethyl-n-butylisoamylammonium iodide*, obtained as a gummy mass from methyl*iso*amylaniline and *n*-butyl iodide, and also from methyl-*n*-butylaniline and *iso*amyl iodide; *platinichloride*, needles, m. p. 191—192°; the hydroxide on decomposition gives methyl*iso*amylaniline.   D. F. T.

Esters Derived from Cyclanols and Acids of the Formic Acid Series. JEAN B. SENDERENS and JEAN ABOULENC (*Compt. rend.*, 1912, 155, 1012—1014).—By a method previously described (A., 1912, i, 694) a series of esters has been prepared from *cyclo*hexanol and the three methyl *cyclo*hexanols and formic, acetic, propionic, butyric, *iso*butyric, and *iso*valeric acids. They are all colourless liquids with a pleasant odour, and are not affected by light, save the o-methyl*cyclo*hexyl esters, which turn slightly yellow on prolonged exposure. The following physical constants were determined. The b. p.'s are all at 750—753 mm.:

	cycloHexyl.		Methylcyclohexyl.							
			Ortho.			Meta.			Para.		
	b. p.	D_4^0	b. p.	D_4^0	n_D^{18}	b. p.	D_4^0	n_D^{18}	b. p.	D_4^0	n_D^{15}
Formate	162·5°	1·0057	173·0°	0 9813	—	176 5°	0·9775	—	177·5°	0·9761	—
Acetate	174·0	0·9854	184 5	0·9636	—	187·5	0·9592	—	188 5	0·9578	—
Propionate ...	193·0	0·9718	203·0	0·9548	1·444	206·0	0·9509	1·442	207·0	0·9492	1·4425
Butyrate	212·0	0·9572	221·5	0·9443	1·445	224·5	0 9403	1·4435	225·5	0·9386	1·443
isoButyrate...	204 0	0·9489	212·5	0·9364	1·441	215·0	0·9318	1·440	216·0	0·9304	1·4395
isoValerate...	223·0	0·9425	231·5	0·9316	1·444	234·0	0·9275	1·4425	235·0	0·9262	1·4425

In passing up the acid series there is an increase of 18·5—19° in the b. p. from one homologue to the next higher, except in the case of the formates, whilst the densities decrease, but in an irregular manner.

W. G.

Esterification of Cyclanols by Aromatic Acids. JEAN B. SENDERENS and JEAN ABOULENC (*Compt. rend.*, 1912, 155, 1254—1256). —Applying the method used for fatty acids (A., 1912, i, 694) to aromatic acids having the carboxyl group attached to the benzene nucleus, in no case was an ester obtained, but the cyclohexanol was always converted into cyclohexene. If, however, the carboxyl group is in the side-chain, condensation readily occurred, and the following esters were prepared:

cycloHexyl phenylacetate, b. p. 180·5°, D_0^0 1·0535, n_D^{13} 1·518.

cycloHexyl phenylpropionate, b. p. 193·5°, D_0^0 1·0432, n_D^{13} 1·515.

o-Methylcyclohexyl phenylacetate, b. p. 186°, D_0^0 1·0374, n_D^{13} 1·512; the meta-isomeride, b. p. 188°, D_0^0 1·0323, n_D^{13} 1·510; and the para-isomeride, b. p. 188·5°, D_4^0 1·0316, n_D^{13} 1·509.

o-Methylcyclohexyl phenylpropionate, b. p. 198·5°, D_0^0 1·0286, n_D^{13} 1·510; the meta-isomeride, b. p. 200°, D_0^0 1·0235, n_n^{13} 1·508; and the para-isomeride, b. p. 200·5°, D_4^0 1·0235, n_D^{13} 1·507.

Menthyl phenylacetate, an oily liquid, b. p. 205·5°/25 mm., D_4^{17} 0·9887.

Menthyl phenylpropionate, needles, m. p. 28·5°, b. p. 216°/25 mm.

W. G.

Action of Potassium Hydroxide on cycloHexanol; Synthesis of cycloHexylcyclohexanol and of Dicyclohexylcyclohexanol. MARCEL GUERBET (*Compt. rend.*, 1912, 155, 1156—1159. Compare A., 1912, i, 67, 154).—cycloHexanol, like other secondary alcohols, undergoes condensation when heated at 230° with potassium hydroxide, some oxidation also occurring with the formation of potassium salts of acids. The following products were obtained by this method:

2-cycloHexyl-3-cyclohexanol, $\begin{array}{c}CH_2 \cdot CH_2 \cdot CH \cdot C_6H_{11} \\ CH_2 \cdot CH_2 \cdot CH \cdot OH\end{array}$, a colourless, oily liquid, b. p. 178—180°/55 mm., D_0^0 0 9950, which yields an acetate, a colourless liquid with a pleasant odour, b. p. 188—190°/52 mm. On oxidation with chromic acid the alcohol is converted into 2-cyclo-

hexyl-3-cyclo*hexanone*, $C_6H_{11}\cdot C_6H_9O$, a colourless liquid, b. p. 176—178°/ 54 mm., yielding an *oxime*, m. p. 102°, and a *semicarbazone*, m. p. 149—150°.

A product of further condensation is 2-*dicyclohexyl*-3-cyclo*hexanol*,

$\begin{array}{l}CH_2\cdot CH_2\cdot CH\cdot C_6H_{10}\cdot C_6H_{11}\\ CH_2\cdot CH_2\cdot CH\cdot OH\end{array}$, prismatic crystals, m. p. 124°.

The acids obtained due to a secondary reaction are hexoic acid, b. p. 204—207°, and cyclo*hexylcyclohexanoic acid*, $C_6H_{11}\cdot C_6H_{11}O_2$ (?), a colourless, oily liquid, b. p. 218—220°/69 mm., D_4^0 1·010, yielding a *barium* salt, crystallising from alcohol. W. G.

Catalytic Action. V. Comparison of the Action of Various Catalysts III. Acetylation of *o* Nitrophenol, Carbazole, and Diphenylamine, and Some Observations on *o*-Nitroaniline and Tribromophenol as well as their Acyl Derivatives. JACOB BÖESEKEN (*Rec. trav. chim.*, 1912, 31, 350—366. Compare A., 1911, i, 22).—Further acetylations have been studied in order to find a simple reaction on which quantitative researches on the influence of catalysts may be based. As a rule, the acetylation of primary amines is too complicated, for both mono- and di-acyl compounds are often produced; thus when *o*-nitroaniline is warmed for a quarter of an hour with acetic anhydride and a trace of sulphuric acid or aluminium chloride, the resulting diaceto-*o*-nitranilide contains a little of the mono-derivative.

The case of *s.*-tribromophenol has already been studied by Smith and Orton (T., 1909, 95, 1063), but their method is criticised, for the acetic acid employed may have influenced the catalysts and their estimation of the final products does not seem to have been trustworthy, since the acetate is somewhat saponified on boiling with water. Titration of the alkali required to saponify the acetate is also found unsatisfactory. The solidification points of mixtures of tribromophenol (m. p. 92·5°) with the acetate (m. p. 82°) have therefore been plotted, but the curve is irregular, and indicates the formation of molecular compounds with m. p. about 65°.

In the case of *o*-nitrophenol, however, a simple solidification curve has been obtained, and found to provide the best means of estimating a mixture of the two compounds. The product of the reaction is washed with ice water, extracted with benzene, and the extract is dried and allowed to evaporate at 50°. By this means it is found that *o*-nitrophenol is acetylated by acetic anhydride at 98° to the extent of 92% in about four and a-half hours. Hydrogen chloride has only a feeble influence, for in one and a-half hours and with 50 molecules of the gas per 100, the process is only two-thirds complete, whereas 3 molecules per 100 of aluminium chloride complete the reaction in one and a-half hours, and 3 molecules per 100 of anhydrous ferric chloride do so in ten minutes.

Diphenylamine is so completely acetylated without catalytic agency on heating with acetic anhydride on the steam-bath that the present studies were carried out at 45°, again with the aid of a solidification curve. Fuming sulphuric acid, ferric chloride, aluminium chloride, and acetyl chloride have nearly equal effects, and the conclusion is drawn

that the catalysts have formed compounds with one of the systems already present, and that it is their influence that is being studied. The formation of sulphacetic acid and probably mono- and di-acetyl-sulphuric acids from acetic anhydride and sulphuric acid (Franchimont, A., 1881, 716) is of importance in this connexion, as well as the fact that aluminium chloride and acetic anhydride produce acetyl chloride (see this vol., i, 6).

Since carbazole is unaffected by alcoholic potash, it was found possible to analyse the mixture by titrating the alkali required for the saponification of the acyl derivative. Without a catalyst, scarcely any acetylation has taken place after five hours at 98°, but with a trace of sulphuric acid or with quite minute amounts of ferric chloride, the process is complete in half an hour.   J. C W.

Nitro-derivatives of Diphenylene Oxide and of Phenyl Ether. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1912, [iv], 11, 1011—1014).—An error in the calculation of nitrogen has led to the description of nitro-derivatives of phenyl ether containing more than four nitro-groups (Mailhe and Murat, A., 1912, i, 346), of penta- and hexa-nitrodiphenylene oxides, and of the disulphonic acid derivative of the latter (Mailhe, A., 1912, i, 553). These substances do not exist.   H. W.

m-**Dithiolbenzene (Dithioresorcinol).** THEODOR ZINCKE and OTTO KRUGER (*Ber.*, 1912, 45, 3468—3479).—The *m*-Dithiolbenzene was prepared in the ordinary way from benzene-1 : 3-disulphonyl chloride by reduction with zinc and hydrochloric acid. In order to obtain good yields the zinc sulphinate must first be formed by the action of the zinc on the chloride in alcoholic solution, and afterwards reduced to the mercaptan by the addition of hydrochloric acid and further action of the zinc. If this method of procedure is not adopted, the free sulphinic acid and the mercaptan react with the formation of tetra- or poly-sulphides.

The following derivatives of *m*-dithiolbenzene have been prepared. *Di*-1 : 3-*phenylene disulphide*, $S_2(C_6H_4)_2S_2$, prepared by the action of perhydrol in alkaline alcoholic solution, forms a yellowish-white, amorphous powder. 4 : 6-*Dichloro*-1 : 3-*dichlorothiolbenzene*,
$$C_6H_2Cl_2(SCl)_2,$$
is obtained by chlorination in chloroform solution. It may also be prepared from the benzyl ester. It forms yellow, glistening needles, m. p. 103°, and shows the usual reactions of the arylsulphur chlorides. When warmed with acetone, it gives slender, colourless needles of 4 : 6-*dichloro*-1 : 3-*diacetonylthiolbenzene*, $C_6H_2Cl_2(S\cdot CH_2Ac)_2$, m. p. 97°.

On methylation with methyl sulphate, *m*-dithiolbenzene gives 1 : 3 *dimethylthiolbenzene*, $C_6H_4(SMe)_2$, a strongly refracting liquid with characteristic odour, b. p. 149°/17 mm., which on treatment with 1 : 4-nitric acid in glacial acetic acid solution yields 4-*nitro*-1 : 3-*dimethyl-thiolbenzene*, $NO_2\cdot C_6H_3(SMe)_2$, yellow, glistening needles, m. p. 114°. The disulphoxide is formed at the same time. 1 : 3-*Diethylthiol-benzene*, $C_6H_4(SEt)_2$, is similar to the dimethyl ether, and has b. p.

164°/18—19 mm. 1 : 3-*Dibenzylthiolbenzene*, $C_6H_4(S \cdot CH_2Ph)_2$, crystallises in leaflets, m. p. 50°.

4 : 6-*Dichloro*-1 : 3-*dimethylthiolbenzene*, $C_6H_2Cl_2(SCH_3)_2$, prepared from the dimethyl ether by chlorination in glacial acetic acid solution, crystallises in long, glistening needles, m. p. 123°. When chlorination takes place in chloroform solution, 1 : 3-*ditrichloromethylthiolbenzene*, $C_6H_4(S \cdot CCl_3)_2$, is obtained as crystals, having the m. p. 106°. Under the action of aniline, fission occurs with the formation of dithiolbenzene and triphenylguanidine.

When the dimethyl ether is treated with bromine in chloroform solution, stout, dark, orange needles of 4 : 6-*dibromo*-1 : 3-*dimethylthiolbenzene dibromide*, $C_6H_2Br_2(SMe) \cdot SBr_2Me$, are obtained. When shaken with sodium hydrogen sulphite solution in the presence of chloroform, 4 : 6-*dibromo*-1 : 3-*dimethylthiolbenzene* itself, $C_6H_2Br_2(SMe)_2$, is obtained as colourless, glistening needles, m. p. 142°. The same compound may be obtained from the disulphoxide by treatment with hydrogen bromide. 4 : 6-*Dibromo*-1 : 3-*diethylthiolbenzene tetrabromide*,

$$C_6H_2Br_2(SBr_2 \cdot Et)_2,$$
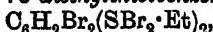
results from the bromination of the diethyl ether in chloroform solution; it forms dark red, in reflected light steel-blue, needles, which readily lose bromine under the action of sodium hydrogen sulphite, giving 4 : 6-*dibromo*-1 : 3-*diethylthiolbenzene*, $C_6H_2Br_2(SEt)_2$, which crystallises in long, silky needles, m. p. 58°.

Oxidation of the dimethyl ether (1 part) with perhydrol (1·5 parts) in glacial acetic acid solution at the ordinary temperature gives white needles of *phenylene*-1 : 3-*dimethyldisulphoxide*, $C_6H_4(SOMe)_2$, m. p. 131°. The corresponding *disulphone*, $C_6H_4(SO_2Me)_2$, is obtained when 3 parts of perhydrol are used and the reaction completed on the water-bath; it crystallises in white, glistening leaflets, and has m. p. 196—197°. The following compounds were obtained in a similar manner: *Phenylene*-1 : 3-*diethyldisulphoxide*, $C_6H_4(SOEt)_2$, is a colourless, oily liquid; the *disulphone*, $C_6H_4(SO_2Et)_2$, forms colourless, clear plates, m. p. 142°. *Phenylene*-1 : 3-*dibenzyldisulphoxide*, $C_6H_4(SO \cdot CH_2Ph)_2$, gives colourless, glistening crystals, m. p. 131°, whilst the *disulphone*, $C_6H_4(SO_2 \cdot CH_2Ph)_2$, forms tabular crystals, m. p. 229°. T. S. P.

4 : 4'-**Dithioldiphenyl.** THEODOR ZINCKE and ALEXANDER DAHM (*Ber.*, 1912, 45, 3457—3468).—4 : 4'-Dithioldiphenyl was obtained from benzidine by Leuckart's method (A., 1890, 603), except that the decomposition of the diazoxanthate was carried out in the presence of copper powder, whereby explosions are avoided and better yields obtained. From this compound a number of derivatives have been obtained.

By the action of chlorine on the solution of the dimercaptan or of its benzyl ether in carbon tetrachloride, 4 : 4'-dichlorothioldiphenyl (A., 1911, i, 369) is obtained. This compound loses chlorine on warming with glacial acetic acid, alcohol or dilute alkali, giving a compound which is probably the tetrasulphide, $S_2(C_6H_4 \cdot C_6H_4)_2S_2$. Oxidation with nitric acid or chlorine in glacial acetic acid solution gives the corresponding sulphonyl chloride. On heating with acetone, 4 : 4'-*diacetonylthioldiphenyl*, $C_{12}H_8(S \cdot CH_2Ac)_2$ is obtained in the form

of almost white needles, m. p. 165°. It can also be obtained from the dimercaptan and chloroacetone.

4 : 4'-Dimethylthioldiphenyl, $C_{12}H_8(SMe)_2$ (compare Leuckart, *loc. cit.*), is obtained by methylating the dimercaptan with methyl sulphate; m. p. 185°. The action of chlorine in glacial acetic acid solution gives the diphenyldichlorothiol, but in chloroform solution substitution occurs in the methyl groups, with the formation of 4 : 4'-*di-trichloromethylthioldiphenyl*, $C_{12}H_8(S\cdot CCl_3)_2$, white needles, m. p. 195°. When heated with aniline, triphenylguanidine and diphenyldithol are formed from the di-trichloro-compound.

4 : 4'-Diethylthioldiphenyl, $C_{12}H_8(SEt)_2$ (compare Leuckart, *loc. cit.*), is prepared similarly to the ethyl compound. The action of chlorine in chloroform solution gives a red oil. It forms a *tetrabromide* and *hexaiodide*.

4 : 4'-*Dibenzylthioldiphenyl*, $C_{12}H_8(S\cdot CH_2Ph)_2$, forms white, glistening, leaflets, m. p. 198—199°. Chlorination in chloroform solution gives benzylidene chloride and the dichlorothioldiphenyl.

4 : 4'-*Dimethylthioldiphenyl tetrabromide*, $C_{12}H_8(SMeBr_2)_2$, is obtained as a red, crystalline precipitate by the action of dry hydrogen bromide on the corresponding sulphoxide (see later) in chloroform solution; m. p. 130° (decomp.). Thiosulphate, sodium sulphite, or concentrated alkali eliminates bromine, whilst water or very dilute alkali regenerates the sulphoxide to some extent. The *hexabromide*, $C_{12}H_8(SMeBr_2)_2,Br_2$, prepared from the dimethyl ester by direct addition of bromine in chloroform solution, forms dark red crystals, and has m. p. 90° (decomp.). It behaves similarly to the tetrabromide towards bromine-eliminating agents. The *hexaiodide*, $C_{12}H_8(SMeI_2)_2,I_2$, is prepared similarly to the hexabromide, and has m. p. 198° (decomp.); it forms almost black crystals. It can also be obtained from the disulphoxide and hydrogen iodide. Iodine is eliminated by the usual agents, but the disulphoxide cannot be obtained from it.

4 : 4'-*Diphenyldimethyldisulphoxide*, $C_{12}H_8(SOMe)_2$, prepared from the dimethyl ether by oxidation with hydrogen peroxide or nitric acid (D 1·5), forms white leaflets, m. p. 195°. In glacial acetic acid solution it is reduced by hydrogen bromide or iodide, in contradistinction to its behaviour in chloroform solution (see above). Oxidation with perhydrol gives the *disulphone*, $C_{12}H_8(SO_2Me)_2$, white leaflets, m. p. 302°. The following sulphoxides and sulphones are prepared similarly : 4 : 4'-*Diphenyldiethyldisulphoxide*, $C_{12}H_8(SOEt)_2$, small, colourless needles, m. p. 134°; the *disulphone*, $C_{12}H_8(SO_2Et)_2$, forms white needles, m. p. 187°. 4 : 4'-*Diphenyldibenzyldisulphoxide*, $C_{12}H_8(SO\cdot CH_2Ph)_2$, consists of white needles, m. p. 243°, as also does the *disulphone*, $C_{12}H_8(SO_2\cdot CH_2Ph)_2$, m. p. 320°.   T. S. P.

The Autoxidation of Trinaphthylcarbinol. JULIUS SCHMIDLIN and MAXIMILIAN BERGMAN (*Ber.*, 1912, **45**, 3203—3205).—In reply to Tschitschibabin's criticism (A., 1911, i, 969) that of the two described isomerides of trinaphthylcarbinol (Schmidlin and Massini, A., 1909, i, 563) the more stable is in reality an oxidation product of the other, it is stated that this oxidation product (α-naphthyl-di-αα-naphthafluoryl alcohol) is a distinct substance, which causes a considerable depression

of the m. p. of the stable isomeride and is more easily obtained than the latter.

It has not hitherto been possible to prepare a triarylcarbinol containing only the diphenyl and naphthyl radicles ; bis-diphenylyl ketone and also esters of diphenylcarboxylic acid refuse to react with magnesium naphthyl iodide, also dinaphthyl ketone with magnesium diphenyl bromide. D. F. T.

Preparation of Acetal Condensation Derivatives from Polyhydroxy-alcohols with Aldehydes or Ketones. WALTER GERHARDT (D.R.-P. 253083. Compare Harnitzky and Mentschutkin, *Annalen*, 1865, **136**, 126).—Glycerol benzylidene ether,

$$C_6H_5\cdot CH{<}^O_O{>}C_3H_5\cdot OH,$$
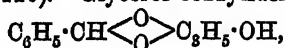
has now been obtained with b. p. 280° and m. p. 84° (compare Fischer, A., 1894, i, 395) by heating glycerol and benzaldehyde together at 135—145°.

The *compound*, $C_{10}H_{12}O_2$, b. p. 113·5—115·5°/14 mm., is obtained from propylene glycol and benzaldehyde at 162° ; and the same aldehyde with trimethylene glycol furnishes *trimethylene glycol benzylidene ether*, $C_{12}H_{10}O_2$, m. p. 50°, b. p. 121—124°/15 mm.

Chlorohydrin benzylidene ether, $C_6H_5\cdot CH{:}O_2{:}C_3H_5Cl$, b. p. 144—146°/14 mm., is prepared from chlorohydrin and benzaldehyde ; glycerol and anisaldehyde yield the *compound*, $C_{11}H_{14}O_4$, b. p. 208—210°/18·5 mm., whilst the *compound*, $C_{11}H_{12}O_5$, m. p. 107—107·5°, is furnished by glycerol and piperonal ; and *acetophenone glycerol*, a viscous liquid, b. p. 156°/16 mm., is obtained from glycerol and acetophenone.

F. M. G. M.

Cubebin. IV. and V. EFISIO MAMELI (*Gazzetta*, 1912, **42**, ii, 546—550, 551—566. Compare A., 1908, i, 20 ; 1909, i, 503).— IV. iso*Cubebin ether* is obtained when cubebin is dissolved in the least quantity of concentrated acetic acid and treated with a small quantity of concentrated sulphuric acid ; on pouring the solution into water, the ether is precipitated. It forms colourless, acicular crystals, m. p. 157°, and has the composition and molecular weight required by the formula $C_{20}H_{18}O_5$. The substance is optically active, having $[\alpha]_D$ 26·02°. It reactions indicate that it is an internal ether.

Although cubebin ether is easily converted into cubebinol by reducing agents, *iso*cubebin ether resists such treatment, but it is converted into cubebinol when boiled with dilute acids.

V. This paper deals with hydroxycubebinic acid and some of its derivatives. The author has investigated the oxidation of cubebin and its derivatives by means of a large number of oxidising agents (hydrogen peroxide, bromine water, iodine water, Fehling's solution, silver oxide, Nessler's reagent, dilute nitric acid, lead nitrate, and lead peroxide, and hydrochloric acid), and has obtained in all cases results analogous to those previously obtained with other oxidising substances by himself and other observers. When, however, cubebin is suspended in strongly alkaline solution of sodium hypobromite at the ordinary temperature, a salt of a new acid, hydroxycubebinic acid, is produced.

The preparation is effected by keeping the reaction mixture in the dark for five or six days; the *sodium* salt which has separated (yield 93—96%) is collected and purified from admixed cubebin, which is insoluble in warm water. When the aqueous solution of this salt is treated with dilute sulphuric acid, the lactone, *cubebinolide*, $C_{20}H_{18}O_6$, is obtained; it forms colourless crystals, m. p. 63—64°, $[a]_D$ +33·69° (in chloroform). This substance behaves in all its reactions as a lactone of a monocarboxylic acid. It dissolves with difficulty in boiling alkalis, yielding the sodium and *potassium* salts of hydroxycubebinic acid. The sodium salt, $C_{20}H_{19}O_7Na$, forms acicular crystals, which melt in their water of crystallisation at 70°; the anhydrous salt has m. p. 205—207°; the salt has no pharmacological action. The other salts were obtained from the sodium salt. The *strontium, magnesium, zinc, cadmium, iron, uranium, copper, cobalt, nickel, lead, manganese, calcium,* $Ca(C_{20}H_{19}O_7)_2$, and *barium,* $Ba(C_{20}H_{19}O_7)_2$, salts were prepared. Indications of the existence of the free acid were observed, but it was not possible to isolate it.

When cubebinolide is treated with magnesium phenyl bromide, a *diphenyl* derivative is obtained, which is to be regarded as the product of dehydration of the glycol which would be expected. This substance crystallises in colourless leaflets, m. p. 136—137°, $[a]_D$ −178·78° (in chloroform), and has the probable formula $C_{32}H_{28}O_5$, although the analytical results do not agree with this very well.

When a methyl-alcoholic solution of cubebinolide is saturated with hydrogen chloride and kept in a sealed vessel, an *ester*, $C_{21}H_{21}O_6Cl$, is obtained; it crystallises in thin laminæ, m. p. 95°, $[a]_D$ +13·89°. When saponified (with strong alkali) it yields a salt of hydroxycubebinic acid.

Oxidation of the lactone with dilute nitric acid gives a *dinitro*-derivative, m. p. 183—184°. The action of bromine on an alcoholic solution of the lactone yields a *dibromo*-derivative, m. p. 137°.

The author gives provisional formulæ to illustrate possible modes of origin of the compounds above described, and their bearing on the constitution of cubebin.   R. V. S.

Hydrolysis of o-Acetoxybenzoates and the Preparation of Calcium o-Acetoxybenzoate. MICHAEL MÁTHÉ (*Chem. Zentr.*, 1912, ii, 431; from *Pharm. Post*, 1912, **45**, 474—476, 481—483).—The calcium salt was prepared by suspending slaked lime in alcohol and adding o-acetoxybenzoic acid, when the salt separated as a coagulated mass, which was washed with alcohol and dried at 40—60°. The sodium salt decomposes in aqueous solution more quickly than the lithium salt, and the latter at first more slowly, but eventually more quickly, than the calcium salt. The lithium salt decomposes when kept in dry powder, and also the calcium salt, but the latter only to a slight extent. In water, all three salts form acetic acid and the corresponding salicylate.   T. A. H.

The Action of Hydrochloric Acid and Potassium Hydroxide on the Lactam of Benzoyldehydracetic Acid. JOH. SCHÖTTLE and PAVEL IV. PETRENKO-KRITTSCHENKO (*Ber.*, 1912, **45**, 3229—3231. Compare A., 1911, i, 1020; 1912, i, 128).—It has already been

observed that the action of concentrated hydrochloric acid and sodium hydroxide solutions on the lactam of benzoyldehydracetic acid produces 2 : 6-diphenyl-4-pyridone-3-carboxylic acid and 2 : 6-diphenyl-4-pyridone respectively.

The action of hydrochloric acid in dilute solution in aqueous alcohol, or of dilute solution of potassium hydroxide in alcohol, gives rise to benzoyldehydracetic acid. This easy removal of nitrogen from the ring does not militate against the structure assumed for the lactam, as the alternative possibility of the position of the nitrogen atom in the side-chain would necessitate the assumption that ammonium chloride (in the action of concentrated solution of acid or alkali) can condense with benzoyldehydracetic acid—an assumption which is not in accord with experimental evidence.

The amide of dehydracetic acid, when heated in a sealed tube with hydrochloric acid at 180°, quantitatively eliminates a molecule of ammonia.   D. F. T.

Nitrogentisic Acids. ALFONS KLEMENC (*Monatsh.*, 1912, 33, 1243—1254).—The stability of gentisic acid (2 : 5-dihydroxybenzoic acid) is so increased by esterification that it can be successfully nitrated, especially if the hydroxyl groups are previously acetylated.

The methyl ester of diacetylgentisic acid, m. p. 62—63·5°, obtained by acetylation of methyl gentisate or by the action of diazomethane on diacetylgentisic acid, when nitrated with fuming nitric acid (D 1·52) and subsequently hydrolysed produces 3-*nitrogentisic acid*, a yellow powder, m. p. 230° (decomp.); *ammonium* salt, brown; the *silver* salt, a yellow, crystalline powder, on treatment with methyl iodide produces the *methyl* ester, yellow needles, m. p. 158° (decomp.), which can also be obtained by direct esterification of the acid by a methyl-alcoholic solution of hydrogen chloride.

Methyl 2-hydroxy-5-methoxybenzoate (Graebe and Martz, A., 1905, i, 702), when nitrated in acetic acid solution with fuming nitric acid, yields *methyl 3-nitro-2-hydroxy-5-methoxybenzoate*, yellow needles (from methyl alcohol), which change to leaflets, m. p. 138—139°; the *potassium* salt, yellow needles, obtained by hydrolysis, on acidification gives 3-*nitro-2-hydroxy-5-methoxybenzoic acid*, yellow needles, m. p. 181°.

Diazomethane acting in ethereal solution converts 3-nitrogentisic acid, and also 3-nitro-2-hydroxy-5-methoxybenzoic acid, into the *methyl* ester (colourless needles, m. p. 71—72°) of 3-*nitro-2 : 5-dimethoxybenzoic acid* (yellow needles, m. p. 181—183°), the acid being obtainable by hydrolysis.

The three nitro-acids described above all give characteristic colours when dissolved in potassium hydroxide solution.   D. F. T.

Preparation of Anthraquinonecarboxylic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 250742).—Anthraquinonecarboxylic acids can be readily prepared by oxidising the corresponding methyl-anthraquinones with nitrous fumes (NO_2 or N_2O_3) at a high tempera-ture in the presence of a suitable solvent, whilst some nitroanthra-quinones can be converted by the action of chlorine into the

corresponding chloroanthraquinones with elimination of the nitro-group.

1-*Chloroanthraquinone-2-carboxylic acid*, yellow needles, is obtained when 1-chloro-2-methylanthraquinone (25 parts) dissolved in 200 parts of trichlorobenzene is treated at 160° with the gases generated from a mixture of arsenious and nitric acids; and the required 1-chloro-2-methylanthraquinone is prepared by treating 1-nitro-2-methylanthraquinone with chlorine at 180°.

1 : 4-*Dichloroanthraquinone-2-carboxylic acid*, citron-yellow needles, is obtained from 1 : 4-dichloro-2-methylanthraquinone, whilst 2-methylanthraquinone furnishes *anthraquinone-2-carboxylic acid*.

F. M. G. M.

Benzalacetoneoxalic Acid [Benzylideneacetylpyruvic Acid]. OTTO MUMM (*Ber.*, 1912, **45**, 3236—3237).—The condensation product of pyruvic acid with benzaldehyde described by Mumm and Bergell (A., 1912, i, 936) as benzylideneacetylpyruvic acid is in reality the isomeric ketoacetylphenylparacone, $CH_3\cdot CO\cdot CH{<}^{CO\cdot CO}_{CHPh}{>}O$ (Ruhemann, T., 1906, **89**, 1236).

It is also formed from ethyl pyruvate and benzaldehyde, either from the sodium salt of the ester or from the free ester in presence of piperidine. E. F. A.

The Combination of Phenolcarboxylic Acids. FERDINAND MAUTHNER (*J. pr. Chem.*, 1912, [ii], **86**, 550—551).—A correction. The products obtained by hydrolysing the compounds described in previous communications (A., 1911, i, 725 ; 1912, i, 267) with alkalis fully confirms the constitutions there given, and, therefore, the author retracts the statements made in his last paper (A., 1912, i, 858).

F. B.

Isomeric and Tautomeric Organo-magnesium Compounds. JULIUS SCHMIDLIN and ANTONIO GARCIA-BANÙS (*Ber.*, 1912, **45**, 3193—3203).—The earlier explanation of the different behaviour of aromatic aldehydes with ordinary and previously heated solutions of magnesium triphenylmethyl chloride (Schmidlin, A., 1906, i, 392 ; 1907, i, 26, 601 ; 1908, i, 239) is adhered to in spite of the criticism of Tschitschibabin (A., 1909, i, 778). In refutation of the latter's criticism, it is stated that his experiments were not of a nature to decide the question, and it is further shown that, although magnesium benzyl chloride cannot be separated into two isomerides, the solution behaves as if it contained a tautomeric mixture of two isomerides, which, it is suggested, represent the normal and quinonoid configurations already assumed for the two forms of magnesium triphenylmethyl chloride.

When magnesium benzyl chloride solution in ether is treated with benzaldehyde, the latter being added in drops, the product is $\alpha\beta$-diphenylethyl alcohol, $CH_2Ph\cdot CHPh\cdot OH$. During the progress of the reaction, the Grignard reagent, which is believed to be an equilibrium mixture of the forms $CH_2{:}C_6H_4{<}^{H}_{MgCl}$ and $CH_2Ph\cdot MgCl$,

has time to rearrange so as to give a theoretical yield of the diphenyl-
ethyl alcohol produced by the latter form. If, however, the Grignard
reagent is gradually introduced into the ethereal solution of
benzaldehyde, both forms enter into reaction, and the product is a
mixture of the above diphenylethyl alcohol with 1 : 3-*diphenyl-*
3 : 4-*dihydro*-2 : 1-*benzopyran* (*diphenylisochroman*),

$$C_6H_4{<}{\stackrel{CHPh\cdot O}{CH_2{-}CHPh}},$$
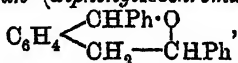
prismatic needles, m. p. 111·5° (corr.), b. p. 237°/9 mm., which dissolve
in concentrated sulphuric acid to a green solution; on oxidation with
potassium permanganate it gives *o*-benzoylbenzoic acid and benzoic
acid, whilst chromic acid produces anthraquinone and benzoic acid.
In the preparation of the above diphenyldihydrobenzopyran, there
was occasionally obtained 1 : 3-*diphenyl*-2 : 1-*benzopyran* (*diphenyliso-*
chromene), $C_6H_4{<}{\stackrel{CHPh\cdot O}{CH{=}CPh}}$, colourless needles, m. p. 125—126°
(corr.); this decolorises bromine and potassium permanganate
solutions, and gives a colourless solution in sulphuric acid; chromic
acid gives the same oxidation products as with the dihydro-compound,
whilst reduction by hydrogen and platinum-black produces the
dihydro-derivative.

With other reagents, the magnesium benzyl chloride undergoes
reaction merely through one of its isomerides; thus the action of
carbon dioxide affects only the normal compound, whereas the
formation of *o*-tolyl alcohol from formaldehyde (Tiffeneau and
Delange, A., 1904, i, 48) depends on the reaction taking place with
the quinonoid isomeride.   D. F. T.

The Action of Ultraviolet Light on *o*-, *m*-, and *p*-Nitro-
benzaldehyde and on Benzaldehyde. ANTON KAILAN (*Monatsh.*,
1912, 33, 1305—1327).—Under the action of ultraviolet light, *o*-nitro-
benzaldehyde, both in alcoholic and benzene solutions, is slowly trans-
formed into *o*-nitrosobenzoic acid (compare Ciamician and Silber, A.,
1901, i, 547), the reaction taking place quicker in quartz than in glass
vessels. The formation of acid from benzaldehyde takes place
similarly. With both aldehydes the acid formation takes place more
rapidly in benzene than in alcoholic solutions. The velocity of
reaction increases with increase in concentration of the aldehyde, but
proportionality does not exist, the increase in velocity being less than
would be expected. Under similar conditions the amount of acid
formed from the *o*-nitrobenzaldehyde is about twice as great as from
the benzaldehyde. When the distance between the source of ultra-
violet light (a mercury lamp) and the reaction vessel is increased, the
diminution in reaction velocity is greater than would be expected from
the inverse-square law. During the reaction a very considerable
portion of the active rays is absorbed.

m- and *p*-Nitrobenzaldehydes, either as the solids or in solution, are
hardly affected by ultraviolet light, the formation of acid being
extremely small. Both solid *o*-nitrobenzaldehyde and liquid benz-
aldehyde are acted on to a considerable extent, in one case 87% of the
benzaldehyde being converted into benzoic acid.

The formation of acid is due principally to oxidation by the oxygen of the air, or by ozone formed by the ultraviolet light; the reaction expressed by the equation : $2Ph \cdot COH + H_2O = Ph \cdot CH_2OH + Ph \cdot CO_2H$, if it takes place at all, plays only a subsidiary part.

In absolute alcoholic solution benzoic acid is not esterified to any appreciable extent under the conditions of experiment, nor does it have any accelerating action on the oxidation of the benzaldehyde, although hydrions, when present in great concentration, may exert such an action.

The temperature-coefficient of the above reactions is very small, as is usually the case in photochemical actions.   T. S. P.

New Synthesis of o-Aldehydophenylnitrosohydroxylamine. OSKAR BAUDISCH (*Ber.*, 1912, **45**, 3429—3430).—A solution of o-nitro-benzaldehyde in 96% alcohol (10 vol.) is diluted with 5 vol. of water, treated with 3 vol. of amyl nitrite and 3 vol. of concentrated aqueous ammonia, and then gradually with zinc dust. The reaction is complete after about fifteen minutes. The mixture is treated with an excess of aqueous copper sulphate, and dilute hydrochloric acid is added carefully with cooling. From the still alkaline solution is obtained a brown, flocculent precipitate, which is removed. The filtrate is rendered distinctly acid, whereby the copper derivative of o-aldehydophenyl-nitrosohydroxylamine is precipitated. After being washed with acetone, the copper salt is converted by aqueous alcoholic potassium hydroxide into the potassium salt, from which o-aldehydophenylnitroso-hydroxylamine, m. p. 52·5°, is liberated by metaphosphoric acid.
                                                                    C. S.

Chemical Action of Light. II. Photo-Oxidation of the Aldehyde Group. I. Terephthalaldehyde. HERMANN SUIDA (*Monatsh.*, 1912, **33**, 1173—1187. Compare A., 1912, i, 117).— Although terephthalaldehyde is very stable in the solid state and in solution in benzene in the dark, its solution undergoes rapid atmospheric oxidation when illuminated by a mercury lamp, and a white, crystalline deposit is formed ; the deposit consists of terephthal-aldehydic acid to the extent of roughly two-thirds, the remainder being terephthalic acid ; the solution from which the crystals have separated gives a peroxide reaction with acidified potassium iodide solution. This oxidation of terephthalaldehyde appears not to occur at all if light is excluded, and it is not accelerated by the presence of nitrobenzene, this substance, indeed, exerting a hindering effect ; a comparison with benzaldehyde seems to indicate that, assuming the supply of oxygen by diffusion to be more than sufficient, the oxidation velocity of each aldehyde group in terephthaldehyde is considerably diminished by the presence of a similar group in the para-position. By interposing solutions of potassium chromate and of quinine sulphate between the solution and the source of light, it is discovered that the effect is mainly due to the ultra-violet rays, but that yellow and red light can cause the oxidation to occur, although only very feebly. Spectrographic examination indicates that the effective rays are from 400 to $300 \mu\mu$.
                                                                    D. F. T.

Catalytic Reduction. VII. The Preparation and Application of Colloidal Platinum Metals. ALADÁR SKITA and W. A. MEYER (*Ber.*, 1912, 45, 3579—3589).—When submitted to the action of free hydrogen, an aqueous alcoholic solution containing an unsaturated aldehyde or ketone with a little palladious chloride and gum arabic undergoes reduction ; colloidal palladium is first formed, which then catalytically accelerates the hydrogenation of the ethylenic linking (Skita, A., 1909, i, 479). If the ethylenic substance has not contain a ketonic or aldehydic group, colloidal palladium is not obtained, but precipitated metal, which, however, is sufficient to aid the reduction of camphene to dihydrocamphene, and of β-phenylvinyl acetate to *β-phenylethyl acetate*, b. p. 109—112°/13 mm., although it fails to reduce double bonds in aromatic nuclei. This action of the carbonyl group in aiding the formation of colloidal palladium is probably due to the formation of a double compound of the ketone or aldehyde with the greater portion of the metallic chloride present (compare Zeisse, *Annalen*, 1840, 33, 29) ; under such conditions it is probable that colloidal particles are first formed which can cause the separation of the rest of the metal in the same form. This is confirmed by the behaviour at the ordinary temperature of a solution of palladious chloride and gum arabic, which, after the addition of a little colloidal palladium, is rapidly reduced by hydrogen to the colloidal metal, whereas if treated directly with hydrogen the metal is slowly precipitated in an insoluble form ; this effect is not merely due to the prevention of supersaturation (Zsigmondy, A., 1906, ii, 679), but is also in part catalytic.

A colloidal solution of palladium can also be obtained by the action of hydrogen on a hot aqueous solution of palladious chloride containing gum arabic ; when a mixture of this solution with an alcoholic feebly acid solution of piperine was treated with hydrogen, tetrahydropiperine (Skita and Franck, A., 1911, i, 1017) was produced.

Solutions of palladious chloride and of potassium platinosochloride containing gum arabic, when treated with sodium carbonate, give palladious and platinous hydroxides in a colloidal condition ; careful evaporation in a vacuum, after dialysis, gives a residue of brown palladious hydroxide or black platinous hydroxide consisting of scales, which readily dissolve in water again. These colloidal hydroxides are well suited to reduction processes, for example, hydrogen reduced an aqueous alcoholic solution of pinene containing a little palladium hydroxide to pinane, and a solution of phorone containing a little platinum hydroxide readily absorbed an amount of hydrogen corresponding with two ethylenic linkings.

Colloidal palladium hydroxide solutions when shaken with hydrogen are reduced to colloidal palladium, and on evaporation in a vacuum black scales are obtained which readily re-dissolve in water; black scales of colloidal platinum can be similarly obtained. These, which can also be prepared directly by reduction of the corresponding chlorides, are again suitable for reduction experiments, *o*-nitroacetophenone and nitrobenzene being easily reduced to the corresponding amino-compounds.

The most satisfactory method for the hydrogenation of an un-

saturated compound is to add to the solution of platinum chloride and gum arabic a trace of a colloidal palladium or platinum solution, and then to act with hydrogen ; the unsaturated substance which may be present from the commencement or introduced later is then easily reduced, for example, quinine yields dihydroquinine, whilst diacetyl-morphine gives *diacetyldihydromorphine,* needles, m. p. 158° (*hydro-chloride,* needles, m. p. above 300°), and cinnamic acid yields β-phenyl-propionic acid.   D. F. T.

Catalytic Reduction. VIII. Hydrogenation of Aldehydes and Ketones, and of Aromatic and Heterocyclic Substances in Colloidal Solutions. ALADAR SKITA and W. A. MEYER (*Ber* , 1912, **45**. 3589—3595. Compare preceding abstract).—It has already been observed that hydrogenation occurs more readily in certain solvents than in others (Fokin, A., 1907, i, 819), and that acetic acid is so suitable that in the presence of platinum black even aromatic substances can be reduced (Willstätter and Hatt, A., 1912, i, 545). By using a colloidal solution of platinum, prepared by one of the methods described (preceding abstract), and applying acetic acid as solvent, it is found possible with hydrogen under an additional pressure of one atmosphere, to reduce toluene to methyl*cyclo*hexane, benzoic acid to *cyclo*hexanecarboxylic acid, naphthalene to decahydro-naphthalene, pyridine to piperidine, heptaldehyde to heptyl alcohol, dihydro*iso*phorone to *trans*-dihydro*iso*phorol, and benzene to *cyclo*-hexane ; in the last two cases only a trace of colloidal platinum was taken with a solution of the substance for reduction, together with chloroplatinic acid, so that the treatment with hydrogen first produced the catalyst, and then reduced the organic substance; the reduction processes generally occupied one to three hours. Quinoline, however, required longer treatment with a rather higher pressure of hydrogen for reduction to decahydroquinoline, and by checking the reduction at the right stage, tetrahydroquinoline could be obtained. A descrip-tion of the apparatus employed is given.

It was not found possible to replace gum arabic satisfactorily by any other protecting colloid.   D. F. T.

Condensation Products of Cyclic Ketones with Acetone. OTTO WALLACH and W. VON RECHENBERG (*Chem. Zentr.,* 1912, ii, 923—924; from *Nachr. K. Ges. Wiss. Gött.,* 1912, 442—445).—Further investigation of the condensation of acetone with 1 : 3-methyl-*cyclo*hexanone (A., 1896, i, 572 ; 1897, i, 425) shows that condensation takes place between the O-atom of the cyclic ketone and hydrogen from the acetone, with the production of compounds having a :CO group in the side-chain, which can be reduced to saturated ketones of the type R·CH₂·COMe, where R is a cyclic radicle. The position of the ethylenic linking is uncertain, but it is probably cyclic.

1:3-*Methylcyclohexylacetone*, b.p. 211·5—212°, D^{25}_{5} 0·8915, n^{m}_{D} 1·4496, obtained by reducing the methyl*cyclo*hexenylacetone produced by condensing 1-methyl*cyclo*hexan-3-one with acetone (*loc. cit.*), is lævo-rotatory, resembles other extra-cyclic ketones in aroma, gives a *semi-*

carbazone, m. p. 154°, and on oxidation with sodium hypobromite yields
1 : 3-methyl*cyclo*hexylacetic acid.　1 : 4-*Methylcyclohexenylacetone*, b. p.
216—217°, D^{21} 0·916, n_D^m 1·4672, has an anise odour, gives a *semi-
carbazone*, m. p. 122—123°, and a liquid *oxime*.　On reduction it yields
1 : 4-*methylcyclohexylacetone*, b. p. 214—215°, D^{21} 0·8930, n_D^m 1·4499.
The latter gives a *semicarbazone*, m. p. 166°, and is oxidised by sodium
hypobromite to 1 : 4-methyl*cyclo*hexylacetic acid.　　　　　　T. A. H.

Action of an Alcoholic Solution of Potassium Hydroxide
on Ketones. II.　Pieter J. Montagne and Jacob Moll van
Charante (*Rec. trav. chim.*, 1912, 31, 298—349.　Compare A., 1908,
i, 988).—The action of alcoholic potash on further derivatives of
benzophenone is described.　It is found that the introduction of an
amino-group into any position in the ring entirely prevents the
reduction to a benzhydrol, but that the presence of methyl, chlorine,
or bromine in the *para*-position, or of chlorine in the *ortho*-position, is
without influence on the reduction.　In the case of the bromo-deriv-
atives it was previously found that 2 : 4 : 6-tribromobenzophenone is
not only reduced, but that it also loses the bromine atoms in 2 and 6
(A., 1910, i, 42).　Studying this detaching influence of the –COPh
group further, it is found that the elimination of bromine occurs
readily in the case of *o*-bromobenzophenone, to a slight extent with
the para-compound, and to a still smaller extent, but certainly, with
the meta-derivative.　The –CHPh·OH group, on the contrary, has no
such detaching influence, the substituted benzhydrols remaining
entirely unchanged when heated with alcoholic potash ; only in the
case of the 4 : 4'-dibromobenzhydrol was there any trace of halogen
removed.　The following benzophenones have been studied : 2-, 3-, and
4-chloro-, 4 : 4'-dichloro-, 2-, 3-, and 4-bromo-, 2 : 4-, 2 : 6-, and 4 : 4'-
dibromo-, 4-iodo-, 2-amino-, 2 : 2'-diamino-, 4 : 4'-didimethylamino-
(Michler's ketone), 2- and 3-methyl-.　Many of these have been
described by Montagne and Koopal (see Koopal, Thesis).

　　2 : 4-Dibromobenzophenone was obtained by the action of benzoyl
chloride and aluminium chloride on 1 : 3-dibromobenzene (Boeseken,
A., 1908, i, 189) and also synthesised as follows : Acetanilide was
converted into 2 : 4-dibromoacetanilide, not by Chattaway's method
(A., 1900, i, 152), since that yielded only *p*-bromoacetanilide, but
according to Mannino and Donato (A., 1908, i, 826).　This was
saponified by 10% potassium hydroxide, and the 2 : 4-dibromoaniline
diazotised.　With amyl nitrite, nitrous acid, or sodium nitrite and
dilute sulphuric acid, a varying quantity of 2 : 4 : 2' : 4'-tetrabromo-
diazoaminobenzene crystallised out, but on warming with water the
mixture gave a good yield of 1 : 3-dibromobenzene.　When mixed
with potassium nitrite and added to concentrated nitric acid, the
formation of a diazoamino compound was prevented (compare O. N.
Witt, A., 1909, i, 855), and on warming the diluted diazotised liquid
with a mixture of copper sulphate and potassium cyanide the
2 : 4-dibromobenzonitrile was obtained.　This was saponified and the
acid converted into the chloride, which with benzene and aluminium
chloride gave the 2 : 4-dibromobenzophenone.　From the mother
liquors of this compound a small amount of 2 : 6-dibromobenzo-

phenone was recovered, the two bromine atoms exerting no steric hindrance, which confirms the author's experience that the Friedel and Crafts's reaction on halogenated benzenes gives rise to ortho- as well as to para-substitution.

2 : 6-Dibromobenzophenone was also synthesised. Sulphanilic acid was converted into dibromoaniline (Orton and Pearson, T., 1908, 93, 735), and this was diazotised as above and converted into 2 : 6-dibromobenzonitrile, which was saponified by 65% sulphuric acid. The amide, m. p. 208·5°, was further treated with 90% sulphuric acid, and the 2 : 6-dibromobenzoic acid was converted into 2 : 6-dibromobenzoyl chloride and this into 2 : 6-*dibromobenzophenone*, $C_6H_3Br_2 \cdot COPh$, which crystallises in very long needles, m. p. 121·5°, b. p. 381°.

4-Aminobenzophenone, m. p. 124°, obtained by the reduction of 4-nitrobenzophenone (Shröter, A., 1909, i, 773) was found to remain unchanged by acetic acid, and was thus distinguished from 4-aminobenzhydrol, m. p. 121°, since the latter gives an acetyl compound, m. p. 153° (Doebner, A., 1882, 507). New benzhydrols obtained by the action of alcoholic potash on the benzophenones are 3-*bromobenzhydrol*, $C_6H_4Br \cdot CHPh \cdot OH$, m. p. 43°, and 3-*methylbenzhydrol*, $C_6H_4Me \cdot CHPh \cdot OH$, slender needles, m. p. 53°.

Detailed crystallographic measurements of the following substances have been made : 4-bromoacetanilide, 2 : 4-dibromoacetanilide, 2 : 4-dibromoaniline, 2 :4-dibromobenzophenone, 2 : 6-dibromobenzamide, and 2-nitrobenzophenone.   J. C. W.

Conversion of Distyryl Ketone into 2 : 6-Diphenylpyrone. DANIEL VORLÄNDER and G. A. MEYER (*Ber*, 1912, 45, 3355—3358).— Distyryl ketone tetrabromide (Claisen and Claparède, A., 1882, 511) when heated in alcoholic solution with a quadrimolecular quantity of potassium hydroxide is converted into a viscous oil, probably the diethoxy-compound, $CO(CH{:}CPh \cdot OEt)$; the substance gives a blood-red solution in sulphuric acid and a gradual brownish-black coloration with ferric chloride solution. When it is heated with hydrochloric acid (D 1·1) under reflux condenser for several hours a mixture of 2 : 6-diphenylpyrone, needles, m. p. 139—140°, with much resinous matter is produced.   D. F. T.

Elimination of Hydrogen from Aromatic Nuclei and Union of the Latter by means of Aluminium Chloride. ROLAND SCHOLL and CHRISTIAN SEER (*Annalen*, 1912, 394, 111—177).— Isolated instances of the union of aromatic nuclei by means of aluminium chloride at elevated temperatures are known, for example, the formation of perylene from 1 : 1'-dinaphthyl (Scholl, Seer, and Weitzenböck, A., 1910, i, 616), of flavanthrene from 2-aminoanthraquinone (Scholl, A., 1907, i, 540), and of *meso*-naphthadianthrone from *meso*-benzdianthrone (Scholl and Mansfeld, A., 1910, i, 494). The authors have now examined this reaction more fully, and find that, by means of anhydrous aluminium chloride at 80—140°, aromatic nuclei can be very satisfactorily united, particularly in the case of aromatic

ketones, where the elimination of the hydrogen is accompanied by the formation of new rings ; thus, 1 : 9-benzanthrone is obtained in 76% yield by heating phenyl a-naphthyl ketone and anhydrous aluminium chloride (5 pts.) at 150° during two and a-half hours. In a similar manner, o-tolyl a-naphthyl ketone yields *5-methyl-1 : 9-benzanthrone* (annexed formula), m. p. 167—168°, yellow needles ; *m*-tolyl a-naphthyl ketone yields 6-*methyl*-1 : *9-benzanthrone*, m. p. 169·5°, yellow needles ; *p* tolyl a-naphthyl ketone yields 7-*methyl*-1 : 9-*benzanthrone*, m. p. 158—159°, yellow needles; *p*-diphenylyl a-naphthyl ketone yields 7-*phenyl*-1 : 9-*benzanthrone*, m. p. 170—171°, yellowish-brown leaflets ; phenyl a-4-hydroxynaphthyl ketone yields 2-*hydroxy*-1 : 9-*benzanthrone*, m. p. 304°, dark red needles (*benzoyl* derivative, m. p. 236°, golden-yellow needles). In the last preparation, 2-*hydroxydihydro*-1 : 9-*benzanthrone*, m. p. 142—143°, yellowish-brown needles, is first formed, it is converted into 2-hydroxy-1 : 9-benzanthrone by prolonged heating or by passing oxygen through its solution in hot aqueous sodium hydroxide.
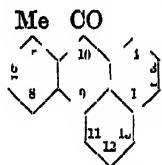
The interaction of naphthalene, o-toluoyl chloride, and aluminium chloride in carbon disulphide leads to the formation of o *tolyl a-naphthyl ketone*, $C_{10}H_7 \cdot CO \cdot C_6H_4Me$, m. p. 64°, b. p. 365—375°. By similar methods, m-*tolyl a-naphthyl ketone*, m. p. 74—75°, and p-*tolyl a-naphthyl ketone*, m. p. 85°, have been prepared. p-*Diphenylyl a-naphthyl ketone*, $C_{10}H_7 \cdot CO \cdot C_6H_4Ph$, m. p. 136—137°, is obtained in a similar manner from a-naphthoyl chloride and diphenyl, or from naphthalene and the *chloride*, m. p. 114—115°, colourless needles, of diphenyl-4-carboxylic acid. *Phenyl a-4-hydroxynaphthyl ketone*, $OH \cdot C_{10}H_6 \cdot COPh$, m. p 164—165°, is obtained from a naphthol and benzoyl chloride by Doebner's method.

o-a-Naphthoylbenzoic acid yields naphthanthraquinone, not the expected 1 : 9-benzanthrone-5-carboxylic acid, by heating with aluminium chloride.

[With Otto von Seybel.]—The interaction of the chloride of anthraquinone-2 carboxylic acid, naphthalene, and aluminium chloride in nitrobenzene at 75—80° for ten hours leads to the formation of a mixture of a-*naphthyl 2-anthraquinonyl ketone*,

$$C_6H_4 {<}^{CO}_{CO}{>} C_6H_3 \cdot CO \cdot C_{10}H_7,$$
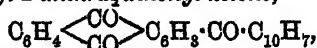
m. p. 166—166·5°, light brown leaflets, and the β-*isomeride*, m. p. 176—177°, citron-yellow needles, which is separated by repeated crystallisation from glacial acetic acid and from pyridine. By heating with aluminium chloride at 100—140° for one hour and again at 140—145° for another hour, the former yields 6 : 7-*phthaloyl*-1 : 9-*benzanthrone* (annexed formula), m. p. 325—326°, dark yellow needles, which, unlike the a-naphthyl anthraquinonyl ketone, forms with alkaline sodium hyposulphite a dark green vat producing on unmordanted cotton green tones changing to yellow in air. The constitution of the
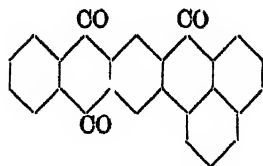
phthaloylbenzanthrone is proved by oxidation with chromic acid, whereby 2 : 3-*phthaloylanthraquinone-5-carboxylic acid*,

$$C_6H_4 <^{CO}_{CO}> C_6H_2 <^{CO}_{CO}> C_6H_3 \cdot CO_2H,$$
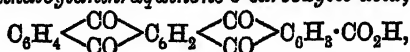
m. p. 338° (decomp.), microcrystalline, yellow needles, is obtained, which is converted by sublimation into Philippi's 2 : 3-phthaloyl-anthraquinone (A., 1911, i, 793). Phthaloylanthraquinonecarboxylic acid forms a greenish-yellow *sodium* salt, which forms with hot alkaline sodium hyposulphite a violet, and finally an orange, solution, changing to blue in air; this solution produces on unmordanted cotton a blue colour which becomes red by treatment with acids.

The interaction of pyrene, benzoyl chloride (rather more than 1 mol.), and aluminium chloride in carbon disulphide for twelve hours at the ordinary temperature, and then for an equal period on the water-bath, leads to the formation of 3-*benzoylpyrene*, m. p. 124—125°, yellow crystals, which is purified by means of the *picrate*, $C_{29}H_{17}O_8N_3$, m. p. 157°, orange needles. By using two or more mols. of benzoyl chloride, a mixture of di- and tri-benzoyl-pyrene is obtained, which is separated readily owing to the slight solubility of the latter in glacial acetic acid. 3 : 5 : 8 *Tri-benzoylpyrene* (annexed formula), m p. 239—240°, crystallises in yellow needles. 3 : 8-*Dibenzoylpyrene*, m. p. 158—160°, slender, yellow needles, yields pyrenequinone by oxidation with aqueous potassium dichromate and sulphuric and acetic acids, and is converted into pyranthrone when mixed with aluminium chloride, placed in a bath previously heated to 155—160°, and kept there for one hour (if the heating is effected gradually, the benzoyl groups are eliminated before the benzanthrone rings are formed). This formation of pyranthrone establishes the direct relation of the substance to pyrene, and also proves the orientation of the benzoyl groups in the dibenzoylpyrene. 3 : 5 : 8-Tribenzoylpyrene is converted into 3-*benzoylpyranthrone*, red-dish-brown, metallic needles, in a similar manner; at a slightly higher temperature, 165—170°, the benzoyl group is eliminated and pyr-anthrone is formed. The interaction of pyrene, α-naphthoyl chloride, and aluminium chloride in carbon disulphide leads to the formation of a nearly quantitative yield of a mixture of 3 : 8- and 3 : 10-di-α-naphthoylpyrene, which is separated by boiling glacial acetic acid, in which the former is in-soluble. 3 : 8-*Di-α-naphthoylpyrene*,
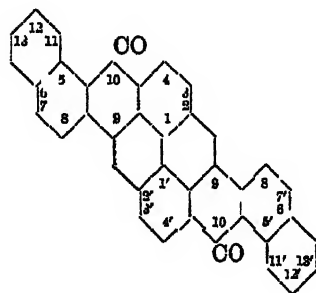
$$C_{38}H_{22}O_2,$$
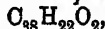
m. p. 271·5—273°, crystallises in micro-scopic, yellow leaflets; the 3 : 10-*isomeride*, m. p. 219—220°, in yellow leaflets. The former and aluminium¹ chloride at 140° for forty minutes yield 5 : 6 : 5′ : 6′-*dibenzpyranthrone* (annexed formula), a brown powder, which forms in hot alkaline sodium hyposulphite a sparingly soluble vat, by which unmordanted cotton is dyed blue, changing to orange-

red in air. In a similar manner, pyrene, β-naphthoyl chloride, and aluminium chloride yield 3 : 10-*di-β-naphthoylpyrene*, m. p. 195·5—197°, yellow crystals (purified by means of the orange yellow *picrate*), and 3 : 8-*di-β-naphthoylpyrene*, m. p. 289°, flattened, yellow needles. The latter and aluminium chloride at 145—155° yield 7 : 8 : 7′ : 8′-*dibenz-pyranthrone*, a brown, indistinctly crystalline powder with green shimmer, which forms a vat behaving like that of the preceding isomeride.

It will be noticed that the action of the preceding acyl chlorides on pyrene in the presence of aluminium chloride yields in each case a pair of diacylpyrenes. One of these is undoubtedly the 3 : 8-diacylpyrene, since it is converted into benz-(or dibenz-)pyranthrone by aluminium chloride. It is known that hydrocarbons such as anthracene and phenanthrene, which are easily oxidised to quinones, are attacked in the Friedel-Crafts reaction by the acid chloride or anhydride in the same positions as by the oxidising agent in the formation of the quinone. Consequently it is probable that pyrene, which forms 3 : 8-diacylpyrenes in the Friedel-Crafts reaction, yields 3 : 8-pyrene-quinone, not 3 : 10-pyrenequinone (Goldschmiedt, A., 1907, i, 310), by oxidation.

The constitution of violanthrone (Bally's violanthrene, A., 1905, i, 237) has been proved by the formation of the substance from 4 : 4′-dibenzoyl-αα-dinaphthyl and aluminium chloride at 95—100°.
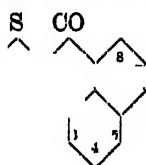
The interaction of naphthalene, pyromucyl chloride, and aluminium chloride in carbon disulphide leads to the formation of (impure) α-*furyl* α-*naphthyl ketone*, $C_4OH_3 \cdot CO \cdot C_{10}H_7$, b. p. 360—365°, which reacts with aluminium chloride to form a brown substance from which individual products have not been isolated. In a similar manner, naphthalene and the chloride of thiophen-2-carboxylic acid, or thiophen and α-naphthoyl chloride, yield α-*thienyl* α-*naphthyl ketone*, $C_4SH_3 \cdot CO \cdot C_{10}H_7$, m. p. 68—69°, b. p. 383°, almost colourless needles, which is converted by aluminium chloride at 140—144° into *benzthiophanthrone*-9 (annexed formula), a brown, crystalline powder; this sinters at 210°, but is not fused at 250°, and yields by fusion with alcoholic potassium hydroxide a dye which is probably the analogue, $C_{30}H_{12}O_2S_2$, of violanthrone.
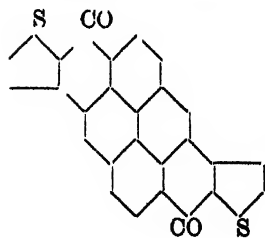
The interaction of pyrene, the chloride of thiophen-2-carboxylic acid, and aluminium chloride in carbon disulphide leads to the formation of 3 : 8-*di-α-thiophenoyl-pyrene*, $C_{26}H_{14}O_2S_2$, m. p. 278—279°, elongated, yellow leaflets, and 3 : 10-*di-α-thio-phenoylpyrene*, m. p. 191—192°, yellow leaflets ; the former and aluminium chloride at 150—158° yield *pyrthiophanthrone* (annexed formula), microscopic, reddish-brown needles. C. S.

Chalkones and Hydrochalkones. II. Guido Bargellini and Mina Finkelstein (*Gazzetta*, 1912, 42, ii, 417—426. Compare Bargellini and Bini, A., 1912, i, 118).—The present paper describes

the reduction of four chalkones to the corresponding hydrochalkones by means of hydrogen in the presence of platinum black or palladium black.

$2' : 4' : 5'$-Trimethoxychalkone (compare Bargellini and Avrutin, A., 1911, i, 68) is conveniently prepared by the original method of preparation of chalkones (Stockhausen and Gattermann, A., 1893, i, 163). If, however, the heating of the mixture of hydroxyquinol trimethyl ether, cinnamyl chloride, and aluminium chloride is prolonged to ten or twelve hours, the principal product is a *substance*, $C_{27}H_{30}O_7$, which forms colourless needles, m. p. 127—128°. This compound dissolves in concentrated sulphuric acid, giving a pale yellow coloration, and does not react with bromine; it probably has the annexed constitution.
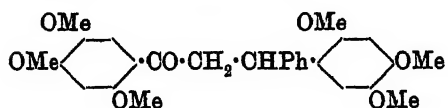
OMe   OMe

OMe⟨   ⟩·CO·CH$_2$·CHPh·⟨   ⟩OMe

OMe   OMe

$2' : 4' : 5'$-*Trimethoxyhydro-chalkone*, $C_{18}H_{20}O_4$, crystallises in colourless needles, m. p. 105—107°; it dissolves in concentrated sulphuric acid, giving a pale yellow coloration.

$3 : 4 : 2' : 4' : 5'$-*Pentamethoxyhydrochalkone*, $C_{20}H_{24}O_6$, forms colourless needles, m. p. 115—117°; it dissolves in concentrated sulphuric acid, giving a pale yellow coloration.

$2'$-*Hydroxy*-$4 : 4'$-*dimethoxyhydrochalkone*, $C_{17}H_{18}O_4$, crystallises in colourless needles, m. p. 58—60°.

$2'$-*Hydroxy*-$3 : 4 : 4'$-*trimethoxyhydrochalkone*, $C_{18}H_{20}O_5$, crystallises in colourless needles, m. p. 78—79°, and dissolves in concentrated sulphuric acid, giving a pale yellow coloration.

Attempts to reduce esperitin were unsuccessful, possibly owing to the hindering action of the free phenolic hydroxyl groups, or perhaps owing to some influence of the solvent.   R. V. S.

Phenylhydroxyketoperinaphthindene. MARCELLO CESARIS (*Gazzetta*, 1912, 42, ii, 453—472).—When phenylacetic acid, naphthalic anhydride, and potassium acetate are heated at 230° for two hours, 1-hydroxy-3-keto-2-phenylperinaphthindene (annexed formula) is formed; it crystallises in iridescent, orange-yellow scales, m. p. 218°, and dissolves in concentrated sulphuric acid, giving an intense yellow coloration. The substance dissolves in alkalis, and is reprecipitated by acids. The *acetyl* derivative, $C_{19}H_{11}O_2Ac$, forms deep yellow needles, m. p. 172—175°. Bromination of hydroxyketophenylperinaphthindene in anhydrous solvents (such as chloroform) yields an unstable *additive product* of the probable formula $C_{19}H_{12}O_2Br_2,HBr$. By the action of water on this compound, or by bromination in aqueous solvents, 2-*bromo*-1 : 3-*diketo*-2-*phenylperinaphthindene* (annexed formula) is obtained; it forms prisms or needles, m. p. 198°. The *anilide*, $C_{19}H_{11}O_2\cdot NHPh$, prepared from the bromo-derivative, crystallises in golden-yellow scales, m. p. 225—227°. When the bromo-derivative is treated with alkalis, hydroxyketophenylperinaphthindene
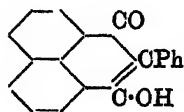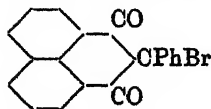
is obtained. The action of hydrogen bromide on hydroxyketophenylperinaphthindene (in chloroform) yields an unstable *compound*, $C_{19}H_{12}O_2HBr$, which begins to melt at 90° and is completely melted at 210°.

Cautious oxidation of hydroxyketophenylperinaphthindene with permanganate yields naphthalic acid, benzoic acid, and traces of an *acid* crystallising in colourless needles, m. p. about 200—202°. Oxidation with potassium dichromate in acetic acid yields a neutral substance, $C_{38}H_{22}O_4$, to which the annexed structure of *bis diketophenylperinaphthindene* is ascribed; it is a straw-coloured, crystalline powder, m. p. about 235—236° (decomp), and it dissolves in concentrated sulphuric acid, giving an intense orange-red coloration.　　　R. V. S.
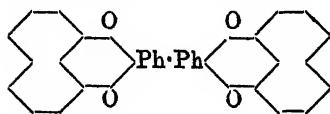
Preparation of α-Chloroanthraquinone. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 252578).—When α-nitroanthraquinone (or its derivatives) is treated with chlorine, this element displaces the α-nitrogroup. Moreover, when 1-nitro-2-methylanthraquinone is similarly treated at high temperatures it furnishes ω-di- with some ω-mono- and ω-tri-chloro-derivatives. 1-Chloroanthraquinone is obtained (in satisfactory yield) when 1-nitroanthraquinone (80 parts) in 400 parts of trichlorobenzene is treated at 160—165° with a stream of chlorine; 1 : 5-dinitroanthraquinone at 190° furnishes 1 : 5-dichloroanthraquinone, and at 160—180° 1-nitro-2-methylanthraquinone yields chiefly ω-1-trichloro-2-methylanthraquinone.　　　F. M. G. M.

Preparation of Condensation Products of the Anthracene Series Containing Sulphur. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 251115).—When negatively substituted anthraquinones which in addition contain one or more auxochrome groups are condensed with arylmercaptols they yield compounds which can be employed as pigments, or for the preparation of dyes.

The *compound* obtained when an alcoholic solution of 4-chloro-1-hydroxy-2-methylanthraquinone (54 parts) containing 13 parts of potassium hydroxide is heated at 100° with p-tolyl mercaptan (25 parts) is a crystalline, violet powder. The following *compounds* obtained in a similar manner are described in the original; from p-tolyl mercaptan with (1) 4-chloro-1-amino-2-methylanthraquinone a glistening, bronze, crystalline powder; (2) with 4-bromo-1-methylaminoanthraquinone, glistening, violet needles; (3) with 1-chloroaminoanthraquinone an orange, crystalline powder; whilst 2-bromo-1-amino-4-hydroxyanthraquinone furnishes 1-*amino-4-hydroxyanthraquinone* 2-p-*tolyl thioether*, violet-brown bronze needles, and 2 : 3-dichloro-1 : 4-diaminoanthraquinone yields 1 : 4-*diaminoanthraquinone* 2 : 3-*dithio*-p-*tolyl ether*, blue needles.　　　F. M. G. M.

Preparation of Anthracene Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252530. Compare A., 1907, i, 1067).—An account of the preparation of *compounds* of cœrthionium type by heating the following anthraquinone thio-ethers with concentrated sulphuric acid at 150—160°: αα'-dianthraquinonyl thio-ether; αβ-dianthraquinonyl thioether; 4 : 4'- or 5 : 5'-dibenzoyldi-

amino-1 : 1'-dianthraquinonyl thioether, whilst the condensation of 1 : 5-dichloroanthraquinone (1 mol.) with 2 mols. of anthraquinone-2-mercaptol (compare A., 1907, i, 1067) furnishes 1 : 5-*anthraquinonedimercaptol-di-2'-anthraquinonyl thioether*.   F. M. G. M.

Binuclear Quinones of the Anthraquinone Group. HANS MEYER, RICHARD BONDY, and ALFRED ECKERT (*Monatsh.*, 1912, 33, 1447—1468).—The supposed oxidation of dihydrodianthrone by amyl nitrite (Padova, A., 1909, i, 167, 655) to dianthrone is apparently a mistake, as the product is a mixture of anthraquinone with unchanged dihydrodianthrone. *Dianthrone*,

$$CO{<}^{C_6H_4}_{C_6H_4}{>}C{=}C{<}^{C_6H_4}_{C_6H_4}{>}CO,$$
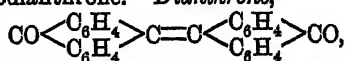
can, however, be easily obtained by the oxidation of dianthranol in alkaline solution with potassium persulphate or hydrogen peroxide; the product, a crystalline powder, is preceded by an intermediate labile green *substance*. If a solution of dianthrone in acetic acid is exposed to sunlight or to the rays from a mercury lamp or an electric arc, it deposits yellow needles of *meso*-naphthadianthrone,

$$CO{<}^{C_6H_3}_{C_6H_3}{>}C{=}C{<}^{C_6H_3}_{C_6H_3}{>}CO$$
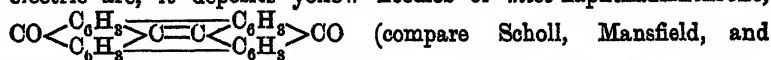
(compare Scholl, Mansfield, and Potschiwauscheg, A., 1910, i, 494); the different properties of the substance described earlier are shown to be due to impurity, as the purified substances give practically identical absorption spectra. The substance gives an orange vat, it dissolves in sulphuric acid to a red fluorescent solution, and is oxidised by chromic acid to anthraquinone. The hydrogen liberated during the above conversion of dianthrone into *meso*-naphthadianthrone is probably largely oxidised by oxygen dissolved in the solvent; also, if an atmosphere of carbon dioxide is used, it is observed that some carbon monoxide is formed; only 95% of the original substance is obtained as *meso*-naphthadianthrone, whilst the solvent is found to contain afterwards about 2% of a volatile *hydrocarbon*, leaflets, m. p. 62—63°, possibly hexahydroanthracene, and also a little anthraquinone.

When anthraquinone is submitted in acetic acid to the action of nascent hydrogen (tin and hydrochloric acid) in intense light, the usual products, anthranol and dianthryl, are accompanied by a considerable quantity of dihydroanthracene.

By stopping the action of light on dianthrone at an early stage, dianthranol is found to be present, and is presumably the primary product from which the other substances above are subsequently formed; this idea is supported by the plentiful formation of diacetyldianthranol when a hot solution of dianthrone in acetic anhydride is exposed to light. Diacetyldianthranol in boiling solution when exposed to light for a considerable time is converted largely into a crystalline *substance*, m. p. circa 300°, and a little *meso*-naphthadianthrone.

Helianthrone (Scholl and Mansfield, *loc. cit.*), dissolved in acetic acid and exposed to light, deposits rhombic leaflets of a substance which on crystallisation from nitrobenzene separates in the characteristic needles of *meso*-naphthadianthrone; the identity of

the product was proved by its absorption spectrum. The yield was over 90%, and was accompanied by a brown, amorphous substance possessing the properties of a hydro-derivative of helianthrone.

<div align="right">D. F. T.</div>

Preparation of Borneol and *iso*Borneol Esters. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252158).—*Borneyl cinnamate*, b. p. 215°/10 mm., when treated with bromine (in carbon tetrachloride solution) yields *borneyl dibromo-β-phenylpropionate*, colourless, glistening crystals, m. p. 73°; this ester can also be prepared by the action of dibromo-β-phenylcinnamoyl chloride on borneol in the presence of pyridine; the corresponding iso*borneyl* ester forms colourless, glistening leaflets, m. p. 69°.

When *borneyl phenylpropiolate*, b. p. 230—235°/19 mm., is treated with bromine it furnishes *borneyl bromocinnamate*, colourless crystals, m. p. 76°, which is also procurable from borneol and bromocinnamoyl chloride.

Borneyl o-*chlorocinnamate*, colourless crystals, m. p. 102—108° (probably a mixture of two isomerides), on bromination yields *borneyl* o-*chloro-aβ-dibromophenylpropionate*, colourless prisms, m. p 91°.

aβ-Dibromo-m-methoxy-β-phenylpropionyl chloride, m. p. 189°, yields a *borneyl* ester, m. p. 63—64°; *borneyl dibromocinnamate* has m. p. 65°, and *borneyl aβ-dibromo β-p-tolylpropionate*, m. p. 90—91°.

These esters are of therapeutic value.

<div align="right">F. M. G. M.</div>

Preparation of Odourless or Faintly Odorous Esters from Valeric Acid and Therapeutically Powerful Alcohols. J. D. RIEDEL (D.R.-P. 252157).—iso*Valerylglycylborneyl* ester, a viscous liquid, b. p. 181°/12 mm., D^{20} 1·027, is prepared by stirring together borneyl chloroacetate and sodium valerate until the separation of sodium chloride is complete; the corresponding iso*borneyl* ester has b. p. 182—183°/12 mm. and D^{15} 1·0318, whilst the iso*valerylglycyl-menthyl* ester has b. p. 197°/19 mm. and D^{16} 0·986.

<div align="right">F. M. G. M.</div>

Δ^4-Menthen-3 one. OTTO WALLACH, RUD. MULLER, and FR. HENJES (*Chem. Zentr.*, 1912, [ii], 922—923 ; from *Nachr. K. Ges. Wiss. Gott.*, 1912, 431—436).—In order to confirm the description and constitution already assigned to Δ^4-menthen-3-one (A., 1908, i, 813), the authors have prepared it from (*a*) Δ^4-menthene, made from 1 : 4-*cyclo*hexanone, and (*b*) *d*-menthene, obtained from menthol, and find that the characters of these two preparations are the same as those already given. The active specimen had $[a]_D^{18}$ - 67·46° in methyl alcohol. The low boiling point of the ketone is probably due to the position of the *iso*propyl side-chain between a :CO group and an ethylenic linking. The latter probably renders reactive the hydrogen atom in position 6, whilst the :CO group confers reactivity on the neighbouring H-atom (position 2), and this joint action explains the formation of a dibenzylidene derivative from this ketone. No thymol is produced on oxidation with ferric chloride in acetic acid.

<div align="right">T. A. H.</div>

Hydrogenation with Platinum Metals as Catalyst. VI. ALADAR SKITA (*Ber.*, 1912, 45, 3312—3318. Compare A., 1911, i, 1017).—Azobenzene in alcoholic solution is readily reduced by

hydrogen under a pressure of two atmospheres in the presence of colloidal palladium with gum arabic as the protecting colloid. The reduction to hydrazobenzene takes place rapidly, whereas the reduction of the hydrazobenzene to aniline proceeds comparatively slowly.

[With W. A. MEYER and JULIUS VON BERGEN.]—Under conditions similar to those used with azobenzene, a-ionone is reduced to *dihydro-a-ionone*, $C_{13}H_{22}O$, which is a liquid, b. p. 121—122°/14 mm., possessing a slight odour of cedar wood, but the characteristic odour of the a-ionone has disappeared. Similarly, β-ionone gives *dihydro-β-ionone*, b. p. 126—129°/12 mm., possessing properties resembling those of the a-compound. Both the dihydro-compounds on further reduction give the same *tetrahydroionone*, $C_{13}H_{24}O$, b. p. 126—127°/13 mm., showing that it is the ethylene linking in the side-chain which is first reduced.

Tiemann (A., 1898, i, 376) has expressed the opinion that ionone acts as a perfume because of the $a\beta$-ethylene linking in the side-chain. If this is so, a dihydroionone which has been hydrogenised in the nucleus, and still contains an $a\beta$-ethylene linking in the side-chain should still be a perfume. To prepare such a compound, dihydro*cyclo*citral was acetylated in tartaric acid solution by a method similar to that used in preparing ψ-ionone from citral and acetone. The *dihydroionone*, $C_{13}H_{22}O$, thus obtained was a pale yellow liquid, b. p. 124—125°/14 mm., and having an odour similar to that of ionone. Since only the latter compound possesses the character of a perfume, the authors propose that the name dihydroionone should be retained for it, whilst the dihydro-compounds obtained from the a- and β-ionones should be termed $1:1:3$-trimethyl-Δ^3- and $1:1:3$-trimethyl-Δ^2-*cyclo*hexenylethyl methyl ketones respectively.

ψ-Ionone when hydrogenised gives *tetrahydro-ψ-ionone*,

$$CMe_2{:}CH{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}COMe,$$
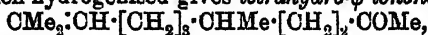
b. p. 126—127°/14 mm

In the unsaturated aldehydes and ketones hitherto examined, with the exception of mesityl oxide (A., 1910, i, 71) and phorone (A., 1909, i, 479), the hydrogenation does not affect the carbonyl group. Acraldehyde also forms an exception, giving allyl alcohol together with propaldehyde.

[With FRIEDRICH NORD.]—The following alkaloids have been hydrogenised by method similar to that used with quinone and cinchonine (A., 1911, i, 1017), the protecting colloid not being used. Quinidine gives *dihydroquinidine*, $C_{20}H_{26}O_2N_2,H_2O$, m. p. 165°, $[a]_D^{20}$ +265·3°; the *methiodide*, $C_{22}H_{27}O_2N_2I$, forms slender, light yellow needles, m. p. 224—225°, and the *phosphate*, $C_{20}H_{29}O_6N_2P$, decomposes at 212°. Cinchonidine gives *dihydrocinchonidine*, $C_{19}H_{24}ON_2$, m. p. 229°, $[a]_D^{20}$ −97·5°, the *methiodide*, $C_{20}H_{27}ON_2I$, and *phosphate*, $C_{19}H_{27}O_3N_2P$, of which have the m. p.'s 248° and 113° respectively. The dihydroquinidine is identical with the naturally-occurring hydroconquinine, and the dihydrocinchonidine with hydrocinchonidine.   T. S. P.

[Glycuronic Acids Produced by the Coupling of Alicyclic Compounds in the Organism.] JUHO HÄMÄLÄINEN (*Skand. Arch. Physiol.*, 1912, 27, 141—226).—See this vol., i, 133.

The Simultaneous Action of Catalysts. VLADIMIR N. IPATIEV (*Ber.*, 1912, **45**, 3205—3218. Compare A., 1911, i, 31).—[With N. MATOV.]—In order to prepare fenchane from fenchone, the latter was first heated with hydrogen under pressure (110 atmos.) for twenty hours at 240°, whereby fenchenol, b. p. 196°/752 mm. and D^{20} 0·9554, was obtained. Attempts to prepare fenchene, which could then be hydrogenised to fenchane, from fenchenol by the fission of water under the catalytic action of alumina at temperatures varying from 210° to 255° gave only very small yields, and the use of the bromo-compound gave no better results. When, however, fenchenol was heated at 215° for twelve to fourteen hours with hydrogen under a pressure of 110 atmos., in the presence of a mixture of nickel oxide and alumina as catalysts, fenchane was obtained directly; $[a]_D$ − 19 83°, D^{17} 0·8766, D^{20} 0·8733, n^{17} 1·45409.

The hydrogenisation of commercial camphene (m. p. 48·5°, b. p. 160—165°/761 mm.) in the presence of nickel oxide at 240° gives *iso*camphane, m. p. 53·5—57°, b. p. 162·5—163·5°/758 mm., D^{19} 0·8457.

Attempts to prepare camphene by the dehydration of borneol in the presence of alumina at 350—360° gave only small yields of a liquid camphene, together with large quantities of oxidation products, the reaction being a very slow one. When, however, borneol (m. p. 208—210°, b. p. 215°, $[a]_D$ + 30·21°) is hydrogenised at 215—220° under 110 atmos. pressure in the presence of a mixture of nickel oxide and alumina, *iso*camphane is obtained, m. p. 63—64·5°, b. p. 164°/757 mm., D^{70} 0·84157, $[a]_D$ − 8·50°. Under similar conditions, *iso*borneol (m. p. 209°, b. p. 211°, $[a]_D$ − 1·82°) also gives rise to *iso*camphane, m. p. 62·5—64°, b. p. 164—164·5°/756·1 mm., D^{70} 0·84293, $[a]_D$ − 2·81°. When heated with alumina alone at 350—360°, *iso*borneol yields small quantities of crystalline camphene, together with considerable quantities of condensation products.

The transformation of cyclic ketones into the saturated hydro-carbons by the combined action of reduction and dehydration catalysts takes place readily, at much lower temperatures than in the reduction of the alcohols. In the presence of a mixture of nickel oxide and alumina at 200°, carvomenthone is readily reduced to menthane by hydrogen under pressure. Similarly, camphor (m. p. 174·5—176°, b. p. 203·5°/743·2 mm., $[a]_D$ + 33·20°) at 200° gives *iso*camphane (m. p. 64·5—65·5, b. p. 164—165°/757 mm., D^{70} 0·8462, $[a]_D$ − 3·95°). Comparison of the physical properties of the various *iso*camphanes prepared from camphene, borneol, *iso*borneol, and camphor shows that they are very similar to each other.

When a mixture of alumina and copper oxide is used instead of alumina and nickel oxide as catalyst, terpene alcohols give rise to unsaturated hydrocarbons. The temperature of dehydration is much lower, being 220° instead of 360°, and in consequence of this lower temperature there is no hydrogenisation of the double linking in the presence of the copper oxide. Under such conditions borneol at 200—220° and a hydrogen pressure of 50 atmos., gives a mixture of solid and liquid camphene, the former having m. p. 60—62·5°, b. p. 156—159°/763 mm., D^{70} 0·85075, and the latter b. p. 155—160°/

763 mm., D^{16} 0·8688, $[a]_D$ 1·61°, n^{16} 1·45819. This liquid camphene yields a chloride, m. p. 140°, and when hydrogenised in the presence of nickel oxide gives liquid *isocamphane*, b. p. 160—165°, D^{18} 0·85204, n^{18} 1·45009.

Under the same conditions as with *corneol*, *isoborneol* gives rise only to a solid camphene, m. p. 53·5°, b. p. 162—167°/766 mm., D^{70} 0·85092, n^{60} 1·44244.

[With O. ROUTALA.]—At 240°, in the presence of a mixture of alumina and copper oxide and under a hydrogen pressure of 20 atmos., 1-methyl*cyclo*hexan-2-ol yields methyl-Δ^1-*cyclo*hexene (compare A., 1911, i, 25), b. p. 107·5—108·5°/759·5 mm., D_4^{18} 0·8063, n^{18} 1·44094. The *nitrosochloride*, C_7H_{12}·NOCl, m. p. 102°, is very unstable, decomposing in a desiccator with the formation of the *oxime*, C_7H_{10}:NOH. The *nitrosate*, $C_7H_{12}O_4N_2$, has m. p. 115°. By the addition of hydrogen bromide in acetic acid solution, 1-*bromomethyl*cyclo*hexane* is obtained as a colourless liquid, b. p. 156—160°, D^{18} 1·2544, n^{18} 1·48168. The action of silver oxide on this compound gives rise to small quantities only of the alcohol, the methyl*cyclo*hexene being regenerated for the most part. With silver acetate, however, the *acetic* ester, $C_9H_{16}O_2$, is readily obtained, b. p. 182—187°, D^{18} 0·9536, n^{18} 1·43862, which, on saponification with alcoholic alkali gives 1-*methyl*cyclo*hexan-1-ol*, $C_7H_{14}O$, b. p. 159—164°/759 mm., D^{18} 0·9417, n^{18} 1·45179.

Attempts to prepare the bromide from 1-methyl*cyclo*hexan-2-ol by the action of phosphorus tribromide were unsuccessful, owing to the ready fission of hydrogen bromide.

To explain the greater catalytic effect of the combined catalysts, it is assumed that a labile complex, for example, NiO,Al_2O_3, is formed as an intermediate product, and then decomposes, giving the components in the nascent state. The combined action of the catalysts is called "hydrolytic reduction." T. S. P.

Constituents of Ethereal Oils. The Sesquiterpene Selinene and its Derivatives. FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1912, 45, 3301—3307. Compare Schimmel, A., 1910, i, 328).— Selinene, $C_{15}H_{24}$, the sesquiterpene from celery seed oil, which has b. p. 128—132°/11 mm., D^{20} 0·9190, n_D 1·5092, $[a]_D+61°36'$, is shown to be a bicyclic doubly unsaturated hydrocarbon. On reduction with hydrogen in presence of finely divided platinum, or of the dihydrochloride with sodium and alcohol, *tetrahydroselinene*, $C_{15}H_{28}$, is obtained, b. p. 126—128°/10·5 mm., D^{20} 0·8881, n_D 1·48259, $[a]_D+7°$.

When selinene dihydrochloride is treated with calcium hydroxide, one halogen atom is eliminated as hydrogen chloride, and the other replaced by hydroxyl, the alcohol *selinenol*, $C_{15}H_{26}O$, being obtained; it has b. p. 155—163°/19 mm., D^{20} 0·9627, n_D 1·50895, $[a]_D+52°36'$. On reduction, *dihydroselinenol*, crystallising in colourless needles, m. p. 86—87°, is obtained. The preparation of this compound is the best method of detecting selinene. E. F. A.

Extraction of Coffee Oil. VIKTOR GRAFE (*Monatsh.*, 1912, 33, 1389—1406. Compare Erdmann, A., 1902, i, 551).—From a comparison with ordinary coffee beans and beans which have been previously deprived of caffeine, it is found that the latter give less coffee oil, the

shortage being especially in the furfuryl alcohol of the mixture. Beans freed from skin and wax gave practically the same results as ordinary beans, so that the parent substance of the coffee oil must have been still present. It is believed that the treatment preceding the extraction of the caffeine diminishes the content of fibrous matter, and causes partial decomposition of the chlorogenic and coffalic acids; these acids are regarded as the source of the valeric acid in coffee oil, whilst the fibrous matter is the origin of the furfuryl alcohol.

D. F. T.

Desulphuration of Vulcanised Rubber. PAUL ALEXANDER (*Chem. Zeit.*, 1912, 36, 1289—1291, 1340—1342, 1358—1359).—The author has stated previously (*ibid.*, 1910, 34, 789) that it is impossible to remove the combined sulphur from vulcanised rubber without destroying the rubber substance. The work of Hinrichsen and Kindscher (A., 1912, i, 706) having placed this conclusion in doubt, the author has repeated and extended this work.

Para rubber was vulcanised by mixing it with varying quantities (5 to 20 parts) of sulphur and heating at 143° under 4 atmospheres pressure. The products (A—E) were then treated in benzene solution with (1) alcoholic sodium hydroxide; (2) alcoholic sodium hydroxide in presence of zinc, magnesium or calcium, and the materials (A_1A_2, B_1B_2, C_1C_2, etc.) thus obtained examined in comparison with the original products. The results are too numerous to quote, but the most interesting are the "vulcanisation-coefficients" arrived at in three different ways: (1) calculated from the total sulphur, less the sum of the sulphur in the ash and that in the "matter soluble in acetone"; (2) calculated from the sulphur in the "matter insoluble in acetone," less the sulphur in the ash, and (3) the sulphur in the nitrosite prepared from the product under examination. From the whole of his results the author draws the conclusion that the last method gives the true vulcanisation-coefficient, that is, the amount of sulphur which combines with 100 parts of pure rubber. The following general conclusions are drawn: The methods described, which are those of Hinrichsen and Kindscher, do not remove combined sulphur from vulcanised rubber, but actually increase the amount in combination when insufficient sodium hydroxide to combine with all the free sulphur is used. The metals used exert no action in this direction. The whole of the free sulphur is not removed from vulcanised rubber by extraction with acetone, probably because part of it at the temperature of vulcanisation is converted into a modified form, which is insoluble in acetone, but dissolves in alcoholic sodium hydroxide. The products (A_1A_2, etc.) referred to above contain "depolymerised rubber," which is soluble in acetone; this material is produced by the heat applied, and not by the action of the alkali hydroxide or the metals or solvents used. The rest of the paper is polemical in favour of Loewen (A., 1912, ii, 914, 915) against Hinrichsen and Kindscher (A., 1912, i, 1007).

T. A. H.

Resin of Pinus Halepensis. L. REUTTER (*J. Pharm. Chim.*, 1912, [vi], 6, 497—500).—This resin has m. p. 83—85°, acid number

180·75—182·74, saponification number 196·5—199·3, ester number 15·7—16·5, and gives colour reactions similar to those of cholesterol. The portion soluble in ether yields to aqueous ammonium carbonate, *helepinic acid*, $C_{21}H_{40}O_4$, m. p. 73·5—74·5°, and subsequently to aqueous sodium carbonate : (1) *helepinolic acid*, $C_{40}H_{56}O_5$, m. p. 144·2—145·5°, which is crystalline and yields a *silver* salt ; (2) *a-helepinolic acid* $C_{84}H_{50}O_4$, m. p. 80 5—81·5°, which is soluble in alcohol, but yields a lead salt insoluble in that solvent ; (3) *β-helepinolic acid*, $C_{18}H_{28}O_4$, m. p.·80·5—82°, which is soluble in alcohol and yields a *lead* salt also soluble in alcohol, and (4) *heleponic acid*, $C_{18}H_{28}O_2$, m. ,p. 156—157°, separating from methyl alcohol in crystals. The resin also contains 14·4% of volatile oil (compare Tschirch and Schulz, A., 1907, i, 544).

T. A. H.

The Resinous Exudation of Pinus Pinea. L. REUTTER (*J. Pharm. Chim*, 1912, [vi], 6, 494—497).—The portion of the oleo-resin soluble in ether yielded on extraction with (1) aqueous ammonium carbonate, *pineic acid*, $C_7H_{14}O_4$, m. p. 99—99·5°, and (2) aqueous sodium carbonate, *pineolic acid*, $C_{18}H_{28}O_8$, m. p. 86°, and a very small amount of a substance giving a precipitate with alcoholic lead acetate. The portion insoluble in ether on steam distillation yielded *pinearesen*, $C_9H_{18}O_4$, m. p. 85°, and a volatile oil, which had an odour recalling that of turpentine, and when kept deposited colourless crystals, m. p. 204°, with an odour similar to that of borneol.

T. A. H.

Chemical Composition of Dulcamara. GEORGES MASSON (*Chem. Zentr.*, 1912, i, 366—367 ; from *Bull. Sci. Pharm.*, 1912, 19, 283—289. Compare Desfosses, *Jahresb.*, 1820, 2, 114 ; Davis, A., 1902, ii, 686).—The aërial portion of dulcamara is free from solanine, but contains in addition to proteins, gums, and reducing sugars, dulcamaretic acid, dulcamaric acid, and solacein (1%). The two acids are both soluble in alcohol, but the first only is soluble in ether, and they can be separated by the use of this solvent.

Dulcamaric acid is a glucosidic saponoid ; it forms a greenish-brown powder, m. p. 190° (decomp.), and yields brown, amorphous salts with alkalis. On hydrolysis with 7% sulphuric acid in alcohol it furnishes (1) *dulcamarigenic acid*, m. p. 160°, and (2) a reducing sugar, which gives a *phenylosazone*, m. p. 196—197°, crystallising from boiling water in slender needles.

Dulcamaretic acid, m. p. 90—92°, is a non-glucosidic saponoid ; it forms a green buttery mass, giving green, amorphous alkali salts. It could not be hydrolysed.

Solacein, m. p. 236—237°, is a nitrogenous glucoside ; it forms a colourless, amorphous mass, soluble in alcohol, but insoluble in ether or water, and reduces auric chloride or silver nitrate on warming, but not Fehling's solution. It yields a yellow *platinichloride*, a stable *sulphate*, and a gelatinous *hydrochloride*. On hydrolysis by acids it furnishes solanidine, m. p. 190°, and a sugar from which a *phenylosazone*, m. p. 171—172°, crystallising in needles from methyl alcohol, was prepared.

Dulcamarin is regarded as an alkali compound of the two acid saponoids.   T. A. H.

Picrotoxin. FRANCESCO ANGELICO (*Gazzetta*, 1912, **42**, ii, 540—545. Compare A., 1911, i, 1003).—When the ketone, $C_{14}H_{16}O_3$ (obtained by the action of hydriodic acid and red phosphorus on picrotoxin, as already described), is heated with concentrated alcoholic potassium hydroxide, a new *compound*, $C_{12}H_{14}O_2$ is obtained in good yield. This substance crystallises in large, colourless needles, m. p. 81°, b. p. 290°; it is volatile with steam and has an odour of celery like the phthalides. It is stable towards oxidisers and reducers, but when heated at 260—280° with three times its weight of powdered potassium hydroxide, it yields acetone and 2 : 3-dimethylbenzoic acid, the barium salt of which gives o-xylene when distilled with barium oxide. When the phthalide, $C_{12}H_{14}O_2$, is oxidised with nitric acid, it yields an *acid*, $C_{12}H_{14}O_4$, of the probable constitution II, whilst when it is oxidised with alkaline potassium permanganate it yields an *acid*, $C_{12}H_{10}O_6,H_2O$, of the probable formula III. This acid gives a fluorescein with resorcinol, and when fused with potassium hydroxide yields acetone and 1 : 2 : 3-benzenetricarboxylic acid. The acid, $C_{12}H_{10}O_6,H_2O$, loses H_2O at about 130°, and gives potassium and silver salts. In view of these reactions, the compound, $C_{12}H_{14}O_2$, probably has the structure indicated in formula I.

(I.)   (II.)   (III.)
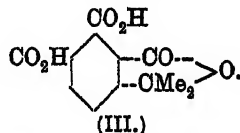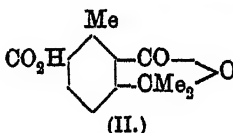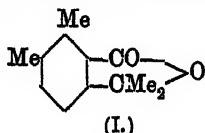
The phthalide has been obtained by other means (but not identified) by Sielisch (A., 1912, i, 886).

The ketone, $C_{14}H_{16}O_3$, from which the phthalide is obtained, also loses acetone when fused with potassium hydroxide, and probably contains the keto-methylenic grouping, since the action on it of amyl nitrite and sodium ethoxide gives an oximino-compound, m. p. 215° (decomp.), which is converted by hydroxylamine into a dioxime. In consequence of these results and of those formerly published, the author regards picrotoxinine and picrotin, not as hydronaphthalene derivatives, but as hydrobenzene derivatives, related to *cyclo*hexene and *cyclo*hexane respectively. He suggests, therefore, the following provisional formulæ for the two substances :
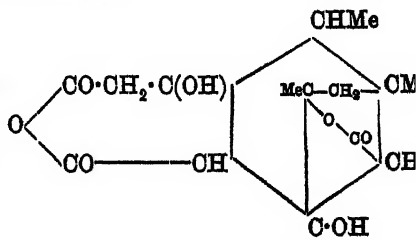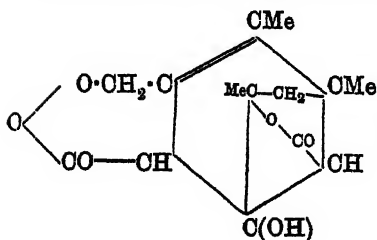
R. V. S.

Picrotinic Acids. PAUL HORRMANN (*Ber.*, 1912, **45**, 3434—3437). —Angelico has given the formula $C_{15}H_{18}O_8$ to α-picrotinic acid and $C_{17}H_{24}O_8$ to its ethyl ester (A., 1910, i, 404). One or other of these formulæ must be wrong. The author shows that α-picrotinic acid has the formula $C_{15}H_{20}O_8$, decomp. 258°, and is identical with Horrmann and Seydel's δ-picrotinic acid (A., 1912, i, 1008). It is not an oxidation product of picrotin, but is produced merely by the addition of water.   C. S.

Tannin. KARL FEIST (*Arch. Pharm.*, 1912, **250**, 668—683).—The author has stated previously that "Turkish" galls contain glucogallic acid and a tannin, which yields dextrose on hydrolysis by acids (A., 1912, i, 566, 888). These two substances are now described.

"Turkish" galls were extracted in turn with chloroform, benzene, and dry ether. The chloroform extract contained chlorophyll, *cyclo*gallipharic acid, and gallic acid. Benzene removed nothing of importance. The ether extract consisted of glucogallic acid and a little tannin. The former was isolated by dissolving the dry extract in acetone, allowing the latter to evaporate, and pouring off the mother liquor as long as amorphous matter separated. Eventually *glucogallic acid* separated in rosettes of greyish needles. It can be prepared in like manner from commercial tannin derived from "Turkish" galls. Glucogallic acid, m. p. 233° (decomp. anhydrous), $[\alpha]_D^{17} + 10\cdot6°$ in acetone, contains when air-dry about 12% of water, and has a molecular weight, when dry, of about 318 as determined by titration (assuming 1 CO_2H group) or by the b. p. method. On hydrolysis by boiling with *N*-sulphuric acid it yields dextrose and gallic acid. It reduces Fehling's solution on boiling, and yields a semi-crystalline *methyl* derivative, m. p. 79°, which, unlike the acid itself, gives no coloration with ferric chloride, and does not reduce Fehling's solution. Glucogallic acid is not decomposed by emulsin, so that it is probably an α-glucoside; it probably does not contain a free ·CHO group.

The partly exhausted galls were next extracted with hot acetone. The *tannin* (designated "Turkish" tannin to distinguish it from that obtained from "Chinese" galls) had $[\alpha]_D + 28\cdot6°$ to $+ 31°$, and molecular weight 615—746 (b. p. method). On treatment with diazomethane in ether, part of it dissolved and was methylated (compare Herzig and Tscherne, A., 1905, i, 354). On hydrolysis the tannin yields dextrose and gallic acid; no glucogallic acid could be obtained as an intermediate product in this hydrolysis (compare Fischer and Freudenberg, A., 1912, i, 471, 887).

The tannin of "Chinese" galls (A., 1912, i, 888) has a molecular weight 899—1045, and is partly methylated on treatment with diazomethane in ether.   T. A. H.

Action of Nitric Acid and Silver Nitrate on Tannin. ROGER DOURIS and A. WIRTH (*Chem. Zentr.*, 1912, ii, 1360; from *Bull. Sci. Pharmacol.*, 1912, **19**, 403—407).—When a solution of tannin is boiled with nitric acid and silver nitrate, silver cyanide is precipitated, the maximum yield occurring with the proportions 2 grams of silver nitrate, 10 c.c. of nitric acid (40° Bé.), and 2 grams of tannin, made up

to 100 c.c. with water. With a mixture of twice this concentration, a very violent reaction results in the formation of oxalic acid. Gallic acid has the same effect, but with pyrogallol or quinol the product is masked by the large amount of reduced silver which is also formed.

<div align="right">J. C. W.</div>

Ratanhine. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1912, 33, 1379—1388). —Ratanhine occurs only exceptionally in ratanhin extract (compare Kreitmair, A., 1874, 1038).

A specimen which came into the author's possession had the composition $C_{10}H_{18}O_8N$, m. p. 252° (decomp.); *hydrochloride*, monoclinic crystals $[a:b:c = 1\cdot0283 : 1 : 0\cdot5111,\ \beta = 103\cdot77°]$; *copper* salt, deep violet prisms; *methyl* ester, m. p. 116—117°, monoclinic prisms $[a:b:c = 0\cdot8096 : 1 : 0\cdot8107,\ \beta = 116\cdot32°]$. On fusion with potassium hydroxide, ratanhine yielded *p*-hydroxybenzoic acid, whilst decomposition by heat gave a *base*; *hydrochloride*, $C_{10}H_{13}ON,HCl$, colourless prisms.

<div align="right">D. F. T.</div>

Degradation of Bilirubin and Bilirubic Acid. HANS FISCHER and HEINRICH ROSE (*Ber.*, 1912, 45, 3274—3280).—Previously only traces of bases have been obtained on reduction of bilirubin. On boiling for fourteen to sixteen hours with acetic acid and hydrogen iodide, cryptopyrrole, $NH{<}^{CH=CMe}_{CMe:CEt}$, is readily obtained. It is left undecided whether hæmopyrrole and phyllopyrrole are also present. The second degradation product, the isomeric phonopyrrolecarboxylic acid, was isolated in relatively considerable quantity. It is readily esterified by means of methyl alcohol and dry hydrogen chloride, a method which is also applicable to phonopyrrolecarboxylic acid. This ester forms a dark brownish-red picrate, whereas the picrate of the isomeric ester is a normal yellow colour.

Bilirubic acid when reduced in a similar manner yields cryptopyrrole in small quantity together with a large proportion of the isomeric phonopyrrolecarboxylic acid; a considerable amount of the bilirubic acid remains unattacked. The results are interpreted as in favour of the formula:

$$\begin{matrix}CEt\cdot CMe\\CMe\cdot NH\end{matrix}{>}C\cdot O\cdot C{<}\begin{matrix}CMe\cdot C\cdot CH_2\cdot CH_2\cdot CO_2H,\\NH-CMe\end{matrix}$$

for bilirubic acid.

Methyl phonopyrrolecarboxylate crystallises in colourless, flat needles, m. p. 57—58°. The *picrate* forms reddish-brown needles with a marked lustre, m. p. 121—122°. The *picrate* of the isomeric *methyl phonopyrrolecarboxylate* crystallises in slender, yellow, concentrically-grouped needles, m. p. 107—108°. The free *ester* obtained from the picrate forms crystals, m. p. 47—48°.

<div align="right">E. F. A.</div>

Bile Pigments. IV. HANS FISCHER and HEINRICH ROSE (*Zeitsch. physiol. Chem.*, 1912, 82, 391—405).—In part already abstracted (preceding abstract). On oxidation of bilirubin after reduction with sodium amalgam, methyl ethylmaleinimide and the oxime of phonopyrrole

carboxylic acid are obtained. This observation makes the existence of a third pyrrole complex in bilirubin probable.

Methylethylmaleinimide is also obtained on oxidation of bilirubic acid together probably with the oxime of phonopyrrolecarboxylic acid.

E. F. A.

Transformation of an Alcohol into a Sulphide or a Peroxide by Hydrogen Sulphide or Hydrogen Peroxide. ROBERT FOSSE (*Compt. rend.*, 1912, 155, 1019—1020).—Xanthhydrol reacts with hydrogen sulphide or hydrogen peroxide as does a basic hydroxide, giving rise respectively to a sulphide and a peroxide.

On passing a stream of hydrogen sulphide into a solution of xanthhydrol in acetic acid a white, microcrystalline deposit of *xanthyl sulphide*, $\left(O{<}{C_6H_4 \atop C_6H_4}{>}CH\right)_2S$, is obtained, which is decomposed by hydrochloric acid, giving hydrogen sulphide and unstable xanthyl chloride. *Xanthyl peroxide*, $\left(O{<}{C_6H_4 \atop C_6H_4}{>}CH\right)_2O_2$, is similarly prepared by the addition of hydrogen peroxide to the acetic acid solution of xanthhydrol. On boiling it with fuming hydrochloric acid, chlorine is evolved and a pyrryl salt is produced. The peroxide gives an orange-yellow solution in a mixture of acetic and hydrochloric acids, which with chlorides or bromides of gold or uranium yields double xanthyl metallic chlorides or bromides.

W. G.

Triphenylmethyl. XXI. Quinocarbonium Salts of the Hydroxyxanthenols. MOSES GOMBERG and C. J. WEST (*J. Amer. Chem. Soc.*, 1912, 34, 1529—1569).—In an earlier paper (A., 1911, i, 737) it was stated that hydroxy- and methoxy-xanthenols yield colourless carbinyl chlorides which are capable of uniting with a metal haloid, a halogen, or hydrogen haloid to form coloured quinocarbonium salts (compare Gomberg and Cone, A., 1910, i, 55, 869). A study has now been made of the salts of *p*-, 1-, 2-, 3-, and -4-hydroxy- and -methoxy-phenylxanthenol and of 3:6-dihydroxyphenylxanthenol.

It has been found that the hydroxy- and methoxy-groups cause a deepening of the colour of the quinonoid derivatives from the yellow of phenylxanthenol to deep red except in the case of the 3-derivatives which are yellow. The presence of these groups increases the stability of the quinonoid compounds, but diminishes that of the benzenoid salts; it also increases the reactivity of the xanthones. The influence of acetoxy- and benzoxy-groups diminishes the tendency of the compounds to tautomerise into the quinonoid form. The constitution of the compounds is discussed.

I. p-*Hydroxyphenylxanthenol Compounds.*—p-*Anisylxanthenol*,

$$OMe{\cdot}C_6H_4{\cdot}C(OH){<}{C_6H_4 \atop C_6H_4}{>}O,$$
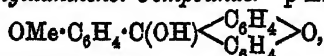
m. p. 120—121°, prepared by adding xanthone to the product of the action of magnesium on *p*-anisyl iodide, separates from benzene in white, prismatic crystals, containing $\frac{1}{2}C_6H_6$, and from ether or acetone in large, monoclinic prisms. p-*Anisylquinoxanthenol chloride*

hydrochloride, $\text{HCl,CHCl·CH:C} \overbrace{\hspace{2.5cm}}^{} \text{O} \atop \text{CH=CH-C:C(C}_6\text{H}_4\text{·OMe)}} \Big\rangle \text{C}_6\text{H}_4$, m. p. 110—115°

(decomp.), prepared by saturating a benzene solution of the xanthenol, to which a little acetyl chloride has been added, with hydrogen chloride, forms dark red crystals. If this salt is suspended in benzene or light petroleum and a current of air passed through the mixture, the hydrogen chloride is removed, and p-*anisylxanthenol chloride,* $\text{OMe·C}_6\text{H}_4\text{·CCl} <^{\text{C}_6\text{H}_4}_{\text{C}_6\text{H}_4}> \text{O}$, m. p. 95—96°, is produced, which forms colourless crystals. When a solution of the chloride in benzene is shaken with molecular silver, an unsaturated compound, analogous to triphenylmethyl, is formed, which on exposure to the air is converted into the *peroxide,* $\left[\text{O} <^{\text{C}_6\text{H}_4}_{\text{C}_6\text{H}_4}> \text{C(C}_6\text{H}_4\text{·OMe)} \right]_2 \text{O}_2$, m. p. 214° (decomp.), obtained as a white, crystalline powder. The following additive compounds of the chloride are described : *ferrichloride,* m. p. 198—199°; *zincichloride,* m. p. 240—241°; *mercurichloride,* m. p. 185—186°; *perbromide,* m. p. 159—163° (decomp.); and *periodide.* p-Anisylxanthenol *ethyl ether,*

$$\text{O} <^{\text{C}_6\text{H}_4}_{\text{C}_6\text{H}_4}> \text{C(OEt)·C}_6\text{H}_4\text{·OMe,}$$
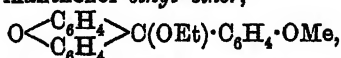
m. p. 156—157°, and *methyl ether,* m. p. 129—130°, form colourless crystals.

p-*Anisylquinoxanthenol bromide hydrobromide* is a dark brown, crystalline substance. The *bromide,* $\text{OMe·C}_6\text{H}_4\text{·CBr} <^{\text{C}_6\text{H}_4}_{\text{C}_6\text{H}_4}> \text{O}$, forms colourless crystals ; its *zincibromide* has m. p. 224—225°; *mercuribromide,* m. p. 192—194°; *perbromide,* m. p. 174—175°, and *periodide,* m. p. 187—189°. p-Methoxyphenylxanthenol *perchlorate,* m. p. 192—193°; hydrogen sulphate, m. p. 117—118°, and *phosphate,* m. p. 124—125°, are described.

p-*Hydroxyphenylxanthenol,* $\text{O} <^{\text{C}_6\text{H}_4}_{\text{C}_6\text{H}_4}> \text{C(OH)·C}_6\text{H}_4\text{·OH,}$ m. p. 149—150° (decomp.), prepared from p-anisylxanthenol by Baeyer's method (A., 1910, i, 251), crystallises in rosettes of colourless needles. The *perchlorate* has m. p. 255—256°, and the *hydrogen sulphate,* m. p. 240—245°. p-*Hydroxyphenylquinoxanthenol chloride hydrochloride,* $\text{O} <^{\text{C}_6\text{H}_4}_{\text{C}_6\text{H}_4}> \text{C:C}_6\text{H}_4 <^{\text{OH}}_{\text{Cl,HCl}}$ or

$$\text{O} <^{\text{C}_6\text{H}_4}_{\text{C}_6\text{H}_4\text{(Cl,HCl)}} > \text{C·C}_6\text{H}_4\text{·OH,}$$
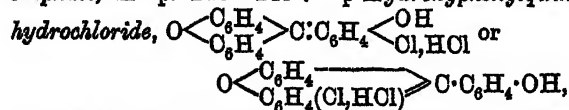
m. p. 235—240°, forms dark red, iridescent plates. p-*Hydroxyphenyl-quinoxanthenol chloride,* m. p. 235—245° (decomp.), is obtained as a red powder by heating the hydrochloride in a vacuum at 130°; its *ferrichloride* has m. p. 156—157°; *zincichloride,* m. p. 222—223°; *mercurichloride,* m. p. 215—216°, and *perbromide,* m. p. 230—235°; the *periodide* is purple. p-*Hydroxyphenylquinoxanthenol bromide,* m. p. 258—260° (decomp.), is a red, crystalline powder. When p-hydroxyphenylxanthenol is heated at 110—120° for two hours, it loses a molecule of water and is converted into *xanthylene-*

quinomethane, $O<^{C_6H_4}_{C_6H_4}>C<^{CH:CH}_{CH:CH}>CO$, m. p. 287—288°, which
has a green colour, and is readily hydrolysed by dilute acid or
alcoholic potassium hydroxide with regeneration of *p*-hydroxyphenyl-
xanthenol.   If the quinone is treated with hydrogen chloride,
p-hydroxyphenylquinoxanthenol chloride hydrochloride is produced,
whilst by the action of hydrogen bromide, *p*-hydroxyphenylquino-
xanthenol bromide is obtained. Acetic anhydride converts the quinone
into *p*-acetoxyphenylxanthenol. The quinone unites with 1 mol. of
methyl sulphate to form a red additive compound which yields
p-anisylxanthenol on hydrolysis.   By the action of phosphorus
pentachloride the quinone is converted into *p*-chlorophenylxanthenol
chloride (Gomberg and Cone, A., 1910, i, 57).

p-*Acetoxyphenylxanthenol,* $O<^{C_6H_4}_{C_6H_4}>C(OH)·C_6H_4·OAc$,   m.   p.
145—146°, obtained by the action of acetic anhydride and sodium
acetate on *p*-hydroxyphenylxanthenol, crystallises in long, slender,
colourless needles. p-*Acetoxyphenylquinoxanthenol chloride hydrochloride,*
$O<^{C_6H_4————}_{C_6H_4(Cl,HCl)}>C·C_6H_4·OAc$, m. p. 118—122° (decomp.), forms
light red crystals. p-*Acetoxyphenylxanthenol chloride,*

$$O<^{C_6H_4}_{C_6H_4}>CCl·C_6H_4·OAc,$$
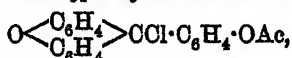
is obtained in colourless crystals; its *ferrichloride* has m. p. 182°;
zincichloride, m. p. 194°; *stannichloride,* m. p. 188°, and *mercuri-
chloride,* m. p. 215°; the *perbromide* has an orange colour. The
peroxide, $\left[O<^{C_6H_4}_{C_6H_4}>C(C_6H_4·OAc)\right]_2O_2$, has m. p. 211—212° (decomp.).

p-*Benzoxyphenylxanthenol,* $O<^{C_6H_4}_{C_6H_4}>C(OH)·C_6H_4·OBz$,   m.   p.
181—182°, forms colourless crystals. p-*Benzoxyphenylquinoxanthenol
chloride hydrochloride,* m. p. 143—145° (decomp.), varies in colour
from yellow to orange-red. p-*Benzoxyphenylxanthenol chloride,* m. p.
175—176°, yields additive *compounds* with ferric chloride, m. p.
204—205°, and with zinc chloride; the *perchlorate* has m. p. 235—236°.
p-*Benzoxyphenylxanthenol peroxide* has m. p. 218—219° (decomp.).

II. 1 - *Hydroxy* - 9 - *phenylxanthenol   Compounds.*—Hydroxy- and
methoxy-xanthones combine much more readily with metal haloids
than xanthone itself. The hydrogen haloid additive compounds are
very unstable, and can only be prepared in absence of water.
1-Methoxyxanthone (Tambor, A., 1910, i, 559) yields the following
compounds: *stannichloride,* m. p. 135—136°; *stannibromide,* m. p.
172—173°; *mercurichloride,* m. p. 183—184°; *mercuribromide,* m. p.
167—168°; *zincichloride* and *zincibromide,* and the *hydrochloride,*
m. p. 110—115°.

1-*Methoxy-9-phenylxanthenol,* $OH·CPh<^{C_6H_4————}_{C_6H_3(OMe)}>O$,   m.   p.
162—163°, prepared by adding 1-methoxyxanthone to a solution of
magnesium phenyl bromide, forms lustrous, colourless needles; its
perchlorate has m. p. 225°. 1-*Methoxy-9-phenylquinoxanthenol chloride*

hydrochloride, $O<^{C_6H_4}_{C_6H_3 \cdot OMe(Cl,HCl)}>CPh$, crystallises in lustrous, purple needles. *1-Methoxy-9-phenylxanthenol chloride,*

$$O<^{C_6H_4}_{C_6H_3(OMe)}>CPhCl,$$
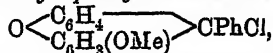
m. p. 160—161°. forms colourless crystals and yields coloured additive compounds with metal haloids. The *peroxide* has m. p. 200—201°.

1-Hydroxy-9-phenylxanthenol, $OH \cdot CPh<^{C_6H_4}_{C_6H_3(OH)}>O$, m. p. 148—150° (decomp.), forms colourless crystals, and yields a dark purple *perchlorate,* m. p. 249—250°. 1-Hydroxy-9-phenylxanthenol chloride could not be isolated, but its *ferrichloride,* m. p. 146—147°, and *stannichloride,* m. p. 185°, were prepared.

III. *2-Hydroxy-9-phenylxanthenol Compounds.*—2-Methoxyxanthone furnishes the following additive compounds: *stannichloride,* m. p. 235—240°; *stannibromide,* m. p. 199—200°; *zincichloride,* m. p. 244—245°; *mercurichloride,* m. p. 200°; *mercuribromide,* m. p. 187—189°; *perchlorate,* m. p. 150—155°. *2-Methoxy-9-phenylquinoxanthenol chloride hydrochloride,* m. p. 140—144° (decomp.), forms bright red crystals. *2-Methoxy-9-phenylxanthenol chloride* has m. p. 198°, and yields a *ferrichloride,* m. p. 123—124°; *zincichloride,* m. p. 197—198°; *mercurichloride; stannichloride,* m. p. 147—149°, and *perbromide.* *2-Methoxy-9-phenylquinoxanthenol bromide hydrobromide* forms deep red crystals and decomposes at 223—224°. *2-Methoxy-9-phenylxanthenol bromide* is colourless, and yields coloured additive compounds with metal haloids; the *perchlorate* and *hydrogen sulphate* have m. p. 193—194° and 110—120° respectively.

2-Hydroxy-9-phenylxanthenol has m. p. 170°. *2-Hydroxy-9-phenylquinoxanthenol chloride hydrochloride,* m. p. about 240°, is obtained as a dark red powder. *2-Hydroxy-9-phenylxanthenol chloride* is colourless, and gives coloured additive compounds with metal haloids. 2-Hydroxy-9-phenylquinoxanthenol bromide (Kropp and Decker, A., 1909, i, 249) yields a *perchlorate,* m. p. about 260°, and *hydrogen sulphate,* m. p. 133—135°.

2-Acetoxy-9-phenylxanthenol, m. p. 151—152°, is a colourless, crystalline substance; the *perchlorate* has m. p. 180—185°. *2-Acetoxy-9-phenylquinoxanthenol chloride hydrochloride,* m. p. 125—129° (decomp.), forms light orange crystals. *2-Acetoxy-9-phenylxanthenol chloride* is colourless and gives coloured additive compounds with metal haloids. The *peroxide,* m. p. 128° (decomp.), forms white crystals.

2-Benzoxy-9-phenylxanthenol, m. p. 205—206°, is colourless; its *perchlorate* has m. p. 210°. *2-Benzoxy-9-phenylquinoxanthenol chloride hydrochloride,* m. p. 147—148°, forms light red crystals. *2-Benzoxy-9-phenylxanthenol chloride,* m. p. 190°, yields coloured additive compounds. The *peroxide* has m. p. 170° (decomp.).

IV. *3-Hydroxy-9-phenylxanthenol Compounds.*—3-Hydroxyxanthone combines readily with metal and hydrogen haloids to form additive compounds. Phenyl-3-methoxyxanthenol (Decker and Fellenberg, A., 1907, i, 1065) has m. p. 125°, and its *perchlorate,* m. p. 215—217°. *3-Methoxy-9-phenylxanthenol chloride* yields a *ferrichloride,* m. p.

163—164°; *zincichloride*, m. p. 200—201°, and *mercurichloride*, m. p. 190°. *3-Methoxy-9-phenylquinoxanthenol bromide hydrobromide*, m. p. 112—115°, is orange-yellow and crystalline. The *zincibromide* of phenyl-3-methoxyxanthenol bromide has m. p. 150—155°.

3-Hydroxy-9-phenylxanthenol cannot be isolated, as it spontaneously loses water with formation of phenylfluorone. *3-Hydroxy-9-phenylquinoxanthenol chloride hydrochloride*, prepared by the action of hydrogen chloride on phenylfluorone, forms yellow crystals. On passing dry air through a solution of this substance in benzene, *3-hydroxy-9-phenylquinoxanthenol chloride*, $O<^{C_6H_4}_{C_6H_3Cl(OH)}>CPh$, m. p. 198—200°, is produced as a yellow solid, which, when treated with molecular silver, is converted into phenylfluorone. *3-Hydroxy-9-phenylquinoxanthenol bromide*, m. p. 238—240°, forms orange needles, and yields a *perchlorate*, m. p. 250°, and hydrogen sulphate, m. p. 201—202°.

V. *4-Hydroxy-9-phenylxanthenol Compounds.*—4-Methoxyxanthone has m. p. 173—174°, and yields a *stannibromide*, m. p. 125—135°; *stannichloride*, m. p. 187—188°; *mercurichloride*, m. p. 204—205°; *perchlorate*, m. p. 160°; and *hydrobromide*. *4-Methoxy-9-phenylquinoxanthenol chloride hydrochloride*, m. p. 144—145°, prepared from phenyl-4-methoxyxanthenol (Baeyer, A., 1910, i, 251), forms dark red, iridescent needles. *4-Methoxy-9-phenylxanthenol chloride*, m. p. 237—238°, is colourless, and yields coloured additive compounds; the *ferrichloride* has m. p. 147—148°; *mercurichloride*, m. p. 205—207°; and the *zincichloride*, m. p. 240—241°. The *peroxide*, m. p. 202° (decomp.), forms colourless crystals. *4-Methoxy-9-phenylquinoxanthenol bromide hydrobromide*, m. p. about 260°, separates in dark red crystals. The colourless bromide was not isolated, but the following coloured compounds were prepared: *zincibromide*, m. p. 234—235°; *mercuribromide*, m. p. 223°; *perbromide*, m. p. 188—189°.

4-Hydroxy-9-phenylxanthenol (Baeyer, *loc. cit.*) yields a *perchlorate*, m. p. 248—249°. *4-Hydroxy-9-phenylquinoxanthenol chloride hydrochloride*, m. p. 210—211°, forms dark red crystals. *4-Hydroxy-9-phenylquinoxanthenol chloride* has m. p. 200—201°, and the corresponding *bromide*, m. p. 261—262°.

4-Acetoxy-9-phenylxanthenol, m. p. 127—128°, crystallises in colourless needles; its *perchlorate* has m. p. 190°. *4-Acetoxy-9-phenylquinoxanthenol chloride hydrochloride* is an orange-red substance, which, when left in a desiccator, loses hydrogen chloride with formation of the colourless *4-acetoxy-9-phenylxanthenol chloride*, m. p. 134—135°; this compound gives a *ferrichloride*, m. p. 136—137°, and a *zincichloride*, m. p. 160—165°. *4-Acetoxy-9-phenylxanthenol peroxide*, m. p. 145—146°, forms colourless crystals.

4-Benzoxy-9-phenylxanthenol has m. p. 113—115°, and yields a *perchlorate*, m. p. 157—158°. *4-Benzoxy-9-phenylquinoxanthenol chloride hydrochloride*, m. p. 85—90° (decomp.), crystallises in yellow needles. *4-Benzoxy-9-phenylxanthenol chloride*, m. p. 111—112°, is colourless, and gives coloured additive compounds with metal haloids.

VI. *3 : 6-Dihydroxy-9-phenylxanthenol Compounds.*—*3 : 6-Dihydroxy-*

9-*phenylquinoxanthenol chloride*, $O<^{C_6H_4(OH)}_{C_6H_3Cl(OH)}>CPh$, prepared by the action of hydrogen chloride on a solution of phenyl-3-hydroxyfluorone (Kehrmann and Dengler, A., 1908, i, 1002) in nitrobenzene or alcohol, forms yellow crystals containing 1 mol. of the solvent. The pure salt darkens at 250°, but does not melt at 275°. E. G.

The Benzeins of the Xyloquinols. FRIEDRICH KEHRMANN and TH. E. STILLER (*Ber.*, 1912, **45**, 3346—3349).—By modifying the process of preparation used for quinolbenzein chloride (Kehrmann, A., 1910, i, 408) it has been found possible to condense *o*- and *p*-xyloquinols with benzaldehyde.

o-*Xyloquinolbenzein chloride* (2 : 7-*dihydroxy-9-phenyl-3* : 4 : 5 : 6-*tetramethylxanthonium chloride*), $CPh<^{C_6PhMe_2(OH)}_{C_6HMe_2(OH)}>O \cdot Cl$, can be obtained by the careful action of benzaldehyde on a mixture of *o*-xyloquinol with the corresponding quinone in the presence of a mixture of equal parts of acetic acid and sulphuric acid; the *sulphate*, which separates in reddish-brown needles, when dissolved in water and treated with concentrated hydrochloric acid precipitates the chloride in brown needles or granules. The solution of the chloride when treated with sodium acetate solution deposits the free *base* in deep brownish-violet needles, for which the analysis indicates an equimolecular combination of anhydride and carbinol base (compare Kehrmann, *loc. cit.*); *platinichloride*, reddish-brown, crystalline powder. If an alkaline solution of the free base is carefully acidified with acetic acid and shaken with ether, the latter extracts the colourless carbinol base, which with more acetic acid turns yellow on account of the formation of the oxonium salt.

p-Xyloquinol was obtained by the reduction of *p*-xyloquinone prepared by the oxidation of *p*-xylidine (compare Noelting, Witt, and Forel, A., 1886, 57). The quinol was made to condense with benzaldehyde by a process similar to that which proved successful with the ortho-isomeride; the resultant p-*xyloquinolbenzein chloride* (2 : 7-*dihydroxy-9-phenyl-1* : 4 : 5 : 8-*tetramethylxanthonium chloride*), deep red or blackish-brown crystals, on treatment in solution with sodium acetate precipitates the free *base* in bright yellow crystals; *platinichloride*, yellow crystalline powder. Unlike the analogous bases previously obtained, which dissolve in sodium hydroxide with a fleeting violet-colour, this base gives a yellow solution in sodium hydroxide.

D. F. T.

Ethers and Esters of Phthaleins and Benzeins of Orcinol. FRIEDRICH KEHRMANN [with E. ACKER, M. GUNTHER, and J. KNOP] (*Ber.*, 1912, **45**, 3505—3514).—By heating with methyl iodide, a solution of *a*-orcinolphthalein in dilute sodium hydroxide yields *a-orcinolphthalein dimethyl ether*,

$$O<^{C_6H_2Me(OMe)}_{C_6H_2Me(OMe)}>C<^{C_6H_4}_{O}{=}>CO,$$
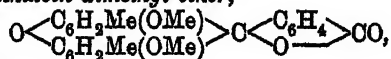
m. p. above 365°, a white, crystalline powder, which exhibits a smaller

tendency than α-orcinolphthalein itself to form oxonium salts. By heating with methyl alcohol and concentrated hydrochloric acid, or by keeping for a month with methyl alcohol saturated with hydrogen chloride, it is converted into the dimethylated *methyl ester oxonium chloride*, $OCl \lessgtr \frac{C_6H_2Me(OMe)}{C_6H_2Me(OMe)} \gtrless C \cdot C_6H_4 \cdot CO_2Me$, reddish-brown needles, which is comparatively easily hydrolysed by water and forms with cold dilute sodium hydroxide a dark blue *substance*, probably the base in the form of a quinol or quinhydrone.

β-Orcinolphthalein is much more prone than the α-isomeride to form oxonium salts, even 10% hydrochloric acid producing an orange-red chloride. By boiling with methyl alcoholic hydrogen chloride, β-orcinolphthalein yields the *methyl ester oxonium chloride*,

$$OCl \lessgtr \frac{C_6H_2Me(OH)}{C_6H_2Me(OH)} \gtrless C \cdot C_6H_4 \cdot CO_2Me,$$
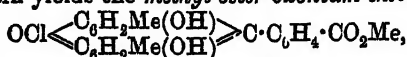
brick-red needles, whilst by treatment with methyl iodide and aqueous sodium hydroxide it yields *β-orcinolphthalein dimethyl ether*,

$$O \lessgtr \frac{C_6H_2Me(OMe)}{C_6H_2Me(OMe)} \gtrless C \lessgtr \frac{C_6H_4}{O} \gtrless CO,$$
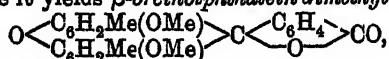
m. p. 247—250°, colourless crystals, which like the dimethylated α-isomeride has little tendency to the formation of stable oxonium salts. The dimethyl ether and methyl alcoholic hydrogen chloride yield the *oxonium chloride*, $OCl \lessgtr \frac{C_6H_2Me(OMe)}{C_6H_2Me(OMe)} \gtrless C \cdot C_6H_4 \cdot CO_2Me$, tufts of yellowish-red needles, which dissolves in cold water without hydrolysis, forming an intensely bitter, orange-yellow solution. The solution is attacked only slowly by sodium acetate or sodium hydrogen carbonate, more rapidly by alkali carbonates or hydroxides, yielding the colourless *carbinol*, from which, immediately after its formation, the orange-yellow salts can be regenerated; the *platinichloride* and *nitrate* are described.

γ-Orcinolphthalein, which is readily freed from its isomerides by means of methyl-alcoholic hydrogen chloride, whereby the pure *chloride* is precipitated in orange-yellow leaflets with a blue shimmer, is not readily etherified or esterified.

Orcinol, benzoic acid, and anhydrous zinc chloride heated at 160—170° for six to seven hours yield a mixture of β - orcinolbenzein, (formula I), orange-red crystals, m. p. 260 — 265°, and
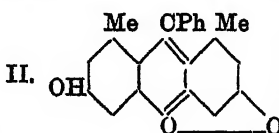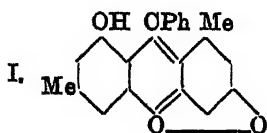
I.

II.

γ-*orcinolbenzein* (formula II), orange-red crystals with a bluish shimmer, m. p. about 270°, the former being isolated as the *alcoholate*, colourless prisms. A concentrated alcoholic solution of this alcoholate and concentrated hydrochloric acid yield, after short boiling, the *oxonium chloride*, $C_{21}H_{17}O_3Cl$, red crystals with a violet shimmer. α-Orcinolbenzein has not been isolated.

By heating with aqueous sodium hydroxide and methyl iodide, β-orcinolbenzein yields the *dimethyl ether*, $C_{23}H_{22}O_4$, m. p. 192—193°,

colourless crystals, which is probably the carbinol,

$$OMe \cdot C_6H_2Me \underset{O}{\overset{CPh(OH)}{<}} C_6H_2Me \cdot OMe.$$
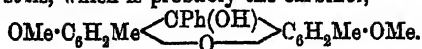
C. S.

Fluorescein. HANS VON LIEBIG (*J. pr. Chem.*, 1912, [ii], **86**, 472—516).—A continuation of previous work (A., 1912, i, 376).

I. *Fluorescein.*—In this section the author gives further details concerning the various modifications of fluorescein, together with an account of the alkali salts of fluorescein and a discussion of their constitution.

Of the five unimolecular yellow varieties of fluorescein, the β- and δ-forms are undoubtedly single chemical individuals, although this may not be the case with the α- and γ-modifications. β-Fluorescein is readily obtained from ordinary fluorescein by boiling (1) with alcoholic hydrogen chloride, (2) with methyl alcoholic potassium hydroxide, and extracting the solution with ether, after acidification with acetic acid. It separates from ether in crystals of the composition $C_{20}H_{12}O_5, C_4H_{10}O$, and on crystallisation from ethyl acetate yields glistening, red leaflets of the βII form, $C_{20}H_{12}O_5$, which becomes red at 280—290° and has m. p. 347°.

A *monosodium* salt of fluorescein having the composition

$$2C_{20}H_{11}O_5Na, 2MeOH, H_2O$$
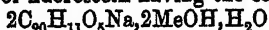
is produced by dissolving fluorescein in methyl-alcoholic sodium hydroxide. It crystallises in lustrous, reddish-yellow leaflets, and when heated increases enormously in volume, after the manner of Pharoah's serpents; the *monopotassium* salt, $C_{20}H_{11}O_5K, MeOH$, prepared in a similar manner, also forms reddish-yellow leaflets.

An anhydrous and alcohol-free *monosodium* salt, $C_{20}H_{13}O_5Na$, is obtained in brownish-red crystals, having a violet lustre, by heating the disodium salt of fluorescein at 220—240°, and subsequently extracting with cold water or hot alcohol; the aqueous or alcoholic extract contains δ-fluorescein, which forms with alcohol, crystals of the composition $4C_{20}H_{12}O_5, EtOH$.

The monosodium salt containing alcohol is at once decomposed by cold water into β-fluorescein and the disodium salt, whilst the alcohol-free salt is insoluble. Further, the anhydrous salt differs from the one containing alcohol in being stable towards cold mineral acids and in yielding a dark brownish-red *sulphate*, $2C_{20}H_{12}O_5, H_2SO_4$, crystallising in leaflets, when boiled with dilute sulphuric acid; the sodium salt containing alcohol yields a *sulphate* of the same composition, but crystallising in yellow leaflets.

A marked difference in the behaviour of the mono- and di-alkali salts of fluorescein has also been observed; the monoalkali salts dissolve in excess of alkali, yielding solutions from which β-fluorescein is liberated by acids, whilst the dialkali salts when subjected to the same treatment give the red variety of fluorescein.

The preparation of a *fluorescein hydrate*, $2C_{20}H_{12}O_5, H_2O$, from the yellow monosodium salt by the action of water is also described; this forms lustrous, light- to violet-red needles, which readily lose their water at the ordinary temperature and then have m. p. 347°.

II. 4:5-*Dinitrofluorescein* (compare Hewitt and Perkins, T., 1900,

77, 1324; Baeyer, A., 1910, i, 249).—The blue tetrapotassium salt of 4:5-dinitrofluorescein, which the author considers to be a p-quinonoid salt of the annexed formula, is obtained by dissolving dinitrofluorescein in aqueous alcoholic potassium hydroxide; it forms bluish-violet needles of the composition
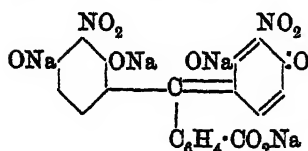
$$C_{20}H_6O_5(NO_2)_2K_4,H_2O,EtOH,$$

and yields blue aqueous solutions, which gradually become light red on dilution, owing to hydrolysis and the formation of a red mono- or di-potassium salt. The light red solutions slowly acquire a yellow colour, a change referred by the author to the loss of water and re-formation of the pyrone ring. The rupture of the ring in these yellow solutions may be effected by alkali hydroxides, but not by sodium carbonate or ammonia.

The *hydrate* of 4:5-dinitrofluorescein, $C_{20}H_{10}O_5(NO_2)_2,H_2O$, prepared by acidifying a fresh aqueous solution of the tetrapotassium salt, crystallises from alcohol in red prisms, m. p. 211—212°.

The *ammonium* salt, $C_{20}H_8O_5(NO_2)_2,2NH_3,H_2O,MeOH$, crystallises in large dark red prisms, m. p. 234° (decomp.); it is obtained by dissolving the dinitrofluorescein in methyl-alcoholic ammonia.

When prepared by the action of potassium hydroxide on 4:5-dinitrofluorescein in aqueous solution, the *dipotassium* salt,
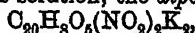
$$C_{20}H_8O_5(NO_2)_2K_2,$$

forms a blackish-red mass of a greenish lustre; in alcoholic solution red crystals of the composition $C_{20}H_8O_5(NO_2)_2K_2,H_2O,EtOH$ are obtained.

Addition of strong aqueous ammonia to 4:5-dinitrofluorescein gives rise to the ammonium salt of the acridine compound described by Reverdin (A., 1897, i, 226); this crystallises in red needles of the composition $2C_{20}H_{10}O_4(NO_2)_2:NH,3NH_3,6H_2O$.

For the purpose of comparison, 2:7-*dinitrofluorescein* (annexed formula) has been prepared and its behaviour towards alkalis studied. It is obtained as a light red, crystalline powder by boiling the nitrate with water, and resembles the parent compound in forming only yellow or red salts, in which the pyrone ring remains intact. The *nitrate*,
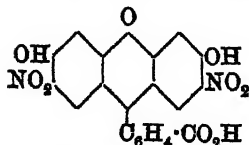
$$C_{20}H_{10}O_5(NO_2)_2,HNO_3,H_2O,$$
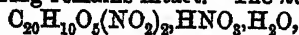
crystallises in yellow needles, and is formed by the action of hot 30—35% nitric acid on fluorescein.

III. *Fluorescein Ethers* (compare A., 1912, i, 376).—In addition to the previously described colourless diethyl ether of m. p. 181°, the action of ethyl sulphate on the disodium salt of fluorescein at 100° gives rise to a new colourless *diethyl ether*, crystallising in needles or prisms, m. p. 234—235°. This resembles in its general behaviour the ether of m. p. 181°, but differs from the latter compound in that it does not form oxonium salts and does not undergo reduction in acid solution. A similar difference is shown by the colourless dimethyl ethers of m. p. 255° and 197° (*loc. cit.*); in both cases the behaviour of the ethers of higher m. p. is in better agreement with the

formula $O<^{C_6H_8(OR)}_{C_6H_3(OR)}>C<^{O---}_{C_6H_4}>CO$ than that of the less fusible ethers, to which, however, this formula has already been assigned.

By hydrolysing the coloured dimethyl ether of m. p. 208° with aqueous sodium hydroxide, Fischer and Hepp (A., 1895, i, 291) obtained a coloured monomethyl ether of m. p. 262°, which closely resembles the monomethyl ether (m. p. 265°) isolated by the author (*loc. cit.*). When hydrolysed with alcoholic potassium hydroxide the dimethyl ether of m. p. 208° yields a colourless *monomethyl ether*, which probably has the constitution $O<^{C_6H_8(OMe)}_{C_6H_3(OH)}>C<^{O---}_{C_6H_4}>CO$. This separates from ethyl acetate in feathery crystals, m. p. 256—257°, forms a dark red *sodium* salt, $C_{21}H_{11}O_5Na$, and on reduction with zinc and glacial acetic acid yields a *substance*, $C_{21}H_{16}O_5$, crystallising in needles, m. p. 205—206°.

The above-mentioned sodium salt corresponds to a *monomethyl ether* of m. p. 266°, which crystallises in lustrous, yellow needles, and is formed by the action of methyl sulphate on an aqueous solution of the disodium salt of fluorescein.

The monomethyl ether of m. p. 265° (or 262°) forms a *sodium* salt of the composition $C_{42}H_{82}O_{14}Na_2$, whilst a coloured *monomethyl ether*, obtained in yellowish-white crystals, m. p. 272°, by methylating fluorescein with methyl iodide and potassium hydroxide in alcoholic solution, yields a blackish-red *sodium* salt having the composition $C_{21}H_{12}O_5Na_2,H_2O$. Since the monomethyl ethers of m. p. 262°, 265°, and 272° do not yield monosodium salts, the conclusion is drawn that these compounds cannot be represented by the formula $O<^{C_6H_4(OMe)}_{C_6H_3(:O)}>C·C_6H_4·CO_2H$.

When warmed with alcohol and hydrochloric acid and the resulting *chloride* heated at 250°, the dimethyl ether of m. p. 208° yields a small amount of the dimethyl ether of m. p. 197°. The latter compound was also obtained in an attempt to prepare a trimethyl ether of fluorescein by the oxidation of the corresponding ether of fluorescin with lead dioxide in glacial acetic acid solution.

Fluorescin trimethyl ether, $C_{23}H_{20}O_5$, prepared by warming fluorescin with strong aqueous potassium hydroxide and methyl sulphate, crystallises in small prisms or leaflets, m. p. 136°. It is accompanied by a *fluorescin monomethyl ether*, $C_{21}H_{16}O_3$, which separates with benzene (1 mol.) in crystals of m. p. 120—125°; in one instance a *substance* was obtained, which crystallised in leaflets, m. p. 204°, and resembled in its behaviour the reduction product of the dimethyl ether of m. p. 197°, mentioned below.

In addition to the dimethyl ethers of m. p. 197°, 208° and 255°, and the monomethyl ether of m. p. 266°, the action of methyl sulphate on an aqueous solution of the disodium salt of fluorescein yields the following substances : (1) a quadrimolecular *monomethyl ether*, $3C_{20}H_{12}O_5,C_{21}H_{14}O_5$, which separates from a mixture of benzene and alcohol in red or brownish-yellow crystals, which become red at 260°, or in crystals containing 4EtOH ; all three modifications have m. p. 330—333°.

(2) A *monomethyl ester*, $O<^{C_6H_8(OH)}_{C_6H_3(:O)}>C·C_6H_4·CO_2Me$, which forms

dark red crystals of a violet lustre, m. p. 282—283°. (3) A *hydrate* of the above ester, $C_{21}H_{14}O_8,H_2O$, crystallising in yellow needles, which become red and melt at 280°.

The monomethyl ester, m. p. 282—283°, is also formed by directly esterifying fluorescein with alcohol and hydrogen chloride, whilst esterification with alcohol and sulphuric acid gives rise to a monomethyl ester of m. p. 252° (compare Feuerstein and Wallach, A., 1901, i, 723).

Methylation of fluorescein by means of methyl iodide and alcoholic potassium hydroxide yields the monomethyl ethers of m. p. 256—257°, 265° and 272°, the dimethyl ether, m. p. 208°, and the quadrimolecular monomethyl ether of m. p. 330—333°.

The *hydrochloride* of the monomethyl ester of m. p. 282—283°, $C_{21}H_{14}O_5,HCl$, forms orange-yellow needles (decomp. 260°).

The monomethyl ether of m. p. 272° yields a *hydrochloride*,
$$3C_{21}H_{14}O_5,2HCl,4H_2O,$$
crystallising in brownish-yellow needles, m. p. 250°.

The products obtained by reducing the ethers of fluorescein, containing a free carboxyl group, with zinc and glacial acetic acid form crystalline compounds with benzene, which is firmly retained until about 110°, whilst those obtained from ethers in which the carboxyl group has been esterified or undergone lactone formation readily lose their benzene below 100°.

The *substance*, $C_{21}H_{16}O_5$, obtained by reducing the monomethyl ether of m. p. 257°, forms needles, m. p. 205—206°; that from the monomethyl ether of m. p. 266° separates in crystals, which become yellow and lose their benzene at 120—125°. The monomethyl ether of m. p. 265° yields a *substance*, $C_{21}H_{16}O_5,2C_6H_6$, which has m. p. 132—133° or 169—170° accordingly as it is dried at 100° or 140°. The *substance* from the monomethyl ether of m. p. 272° has m. p. 173—174°, that from the monomethyl ester of m. p. 282° separates from alcohol in small needles of the composition $C_{21}H_{16}O_5,EtOH$, m. p. 190—191°, and from benzene in crystals which melt at 83—84°, solidifies at a higher temperature, and then melts at 190—191°. The quadrimolecular monomethyl ether on reduction yields a *substance*, $3C_{20}H_{14}O_5,C_{21}H_{16}O_5,H_2O,8C_6H_6$, which loses benzene below 100°, sinters at 220°, and melts at 237—238°.

The *substance*, $C_{22}H_{18}O_5$, obtained from the dimethyl ether of m. p. 197°, forms clusters of needles, m. p. 204°; that from the dimethyl ether of m. p. 208°, stout crystals, m. p. 165°. When oxidised with lead dioxide or hydrogen peroxide in acetic acid solution the last-mentioned reduction product yields a dark red *substance* (decomp. about 200°), which forms dark brown alkali salts, and is probably produced by the oxidation of one of the resorcinol residues, as shown in the annexed formula.
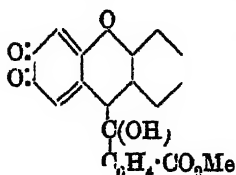
The author suggests that the above results are best explained on the assumption that the ordinary red fluorescein is a polymeride, consisting probably of various di-, ter-, and quadri-molecular combinations as in the case

of resorcinolbenzein, and that the methyl ether of m. p. 330—333°, containing one methyl group to four fluorescein molecules, represents the initial stage in the methylation of the quadrimolecular form, the further methylation resulting in a more or less complete degradation into simple molecules. F. B.

Preparation of Xanthones of the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 251696).—Xanthones of the anthraquinone series are readily prepared by the action of condensing agents on phenyl, naphthyl, or anthraquinonyl ethers of 1-hydroxyanthraquinone-2-carboxylic acids or their substituted derivatives.

1-Phenoxyanthraquinone-2-carboxylic acid, tablets, m. p. 272°, is prepared by the fusion of 1-chloroanthraquinone-2-carboxylic acid (10 parts) with phenol (60 parts) and potassium hydroxide (25 parts) during four hours at 150°. When this product, suspended in trichlorobenzene, is treated with phosphorus pentachloride and the temperature slowly raised, it furnishes the *xanthone* (annexed formula), which separates in yellow, glistening tablets.
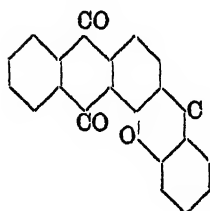
1-Naphthoxyanthraquinone-2-carboxylic acid, yellow tablets, m. p. 262°, is prepared in a similar manner from β-naphthol at 130—140° during two hours; the corresponding *xanthone* is obtained as greenish-yellow leaflets, m. p. above 300°; it dissolves in alkaline hyposulphite with an intense blue, and in concentrated sulphuric acid with a brownish-red, coloration. F. M. G. M.

Preparation of Condensation Products in the Anthracene Series. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 251020). — The *compound*, $C_{20}H_{10}O_3$ (annexed formula), a black powder, is obtained when anthranol and *p*-benzoquinone are boiled together in nitrobenzene -solution; it dissolves in concentrated sulphuric acid with a violet-red coloration.
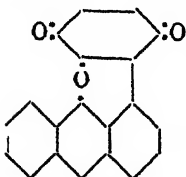
The tinctorial properties of other analogous compounds obtained from *p*-benzoquinone with substituted anthranols are tabulated in the original. F. M. G. M.

Preparation of "7:7'-Diaminothioindigo." FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 252771).—When "7:7'-dinitrothioindigo" (or its substituted derivatives) is reduced with sodium sulphide or dextrose it yields the corresponding "7:7'-diaminothioindigo," a black powder, whilst "5:5'-dichloro-7:7'-dinitrothioindigo" furnishes "5:5'-*dichloro*-7:7'-*diaminothioindigo*," also a black powder. F. M. G. M.

Carpiline, a New Alkaloid from Jaborandi. ÉMILE LÉGER and FERDINAND ROQUES (*Compt. rend.*, 1912, **155**, 1088—1091*).—An

` and *J. Pharm. Chim.*, 1913, [vii], **7**, 5—13.

extract of *Pilcarpus microphyllus*, after the removal of the greater portion of the bases as their hydrochlorides, yields, on precipitating from the mother liquor, the alkaloid *pilocarpiline*, $C_{16}H_{18}O_3N_2$, m. p. 184—185°, $a_D +24°$. It is soluble in chloroform, benzene, and boiling water, and crystallises in colourless prisms. It is a feeble base, its salts with organic acids being dissociated by alcohol, whilst those with mineral acids are stable, all having a bitter taste. It gives a *hydrochloride*, $C_{16}H_{18}O_3N_2,HCl$, colourless prisms; a *sulphate*; a *platinichloride*, $(C_{16}H_{18}O_3N_2)_2,H_2PtCl_6,5H_2O$, crystalline plates, and a *methiodide*, $C_{16}H_{18}O_3N_2,MeI$, small, pale yellow prisms. The base is saturated, since its salts do not reduce potassium permanganate in the cold.

Carpiline contains a lactone group, and thus dissolves in alkali hydroxide solutions, giving compounds of the type *potassium carpilinate*, $C_{12}H_{19}O_4N_2K$, long needles, very soluble in water. The presence of an hydroxyl group is shown by the formation of an amorphous benzoyl derivative which yields *benzoylcarpiline platinichloride*,

$$[C_{16}H_{17}O_3N_2Bz]_2,H_2PtCl_6.$$
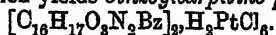
The alkaloid on oxidation with nitric acid yields benzoic acid, and on heating with water at 140° in a sealed tube, it is decomposed, giving benzaldehyde and two amorphous bases, but no hydrogen cyanide.

The alkaloid thus contains the groups $CHPh{:}$, $-OH$, $\genfrac{}{}{0pt}{}{-CO}{-O}$, and the group $C_8H_{11}N_2$, the constitution of which has yet to be elucidated. Carpiline is but slightly toxic, and has not the same effect as pilocarpine on the secretions.   W. G.

Active Principles of Catha Edulis. RALPH STOCKMAN (*Pharm. J.*, 1912, 89, 676—678).

—The leaves and twigs of this plant have long been used in Abyssinia, Somaliland, and Arabia as a stimulant-narcotic. They are now shown to contain at least three alkaloids, cathine, cathidine, and cathinine, to which the characteristic physiological action of the plant is due. By mixing a dry aqueous extract of the plant with slaked lime and extracting with dry alcohol, 0·65 and 0·75% of amorphous alkaloids are obtained from the leaves and twigs respectively. This amorphous mixture appears to consist largely of cathine and its alteration products, but no crystalline alkaloid could be isolated from it. The finely-powdered leaves were extracted completely with cold water or very dilute sulphuric or lactic acid, and the liquor made alkaline and extracted with chloroform, which removed cathine along with much impurity, from which the alkaloid was eventually separated as the sulphate. The ground, partly extracted leaves were then mixed with aqueous sodium carbonate and extracted with ether, which removed cathidine and cathinine; these were separated by taking advantage of the fact that the former is precipitated by sodium carbonate solution from aqueous solutions of its hydrochloride, whilst cathinine remains in solution along with some cathidine.

Cathine sulphate crystallises in colourless needles, is neutral in reaction, has a bitter taste, is precipitated by iodine solution, Mayer's reagent or picric acid, but not by tannin or platinic chloride. *Cathine* crystallises from chloroform and appears to be unstable in presence of

alkalis. Its physiological action on the nervous and muscular systems of the frog is similar to those exerted by morphine and caffeine ; in large doses it paralyses the terminations of the motor nerves.

Cathidine is colourless and amorphous and has a bitter taste ; it gives precipitates with the usual alkaloidal reagents. Cathidine is a muscle poison, and a slight stimulant to the nervous system.

Cathinine sulphate crystallises from water in rosettes of needles, has a bitter taste, and is precipitated by the usual alkaloidal reagents. The free base has only been obtained as a gummy or semi-crystalline mass. Cathinine is less depressant than cathine in its action on the brain, but has a greater stimulant effect on the spinal cord ; it paralyses the terminations of the motor nerves.

All three alkaloids in mammals and man act chiefly on the cerebrum and spinal cord, causing stimulation or much excitement according to the dose ; cathine produces drowsiness at first. The leaves also contain a fermentable sugar, tannin, caoutchouc, wax, and volatile oil.

<div align="right">T. A. H.</div>

Preparation of Esters of Hydroquinine. VEREINIGTE CHININ-FABRIKEN ZIMMER & Co. (D.R.-P. 251936. Compare A., 1912, i, 1013).

—It is found that the hydroquinine esters described previously can be most easily prepared in the presence of either finely divided metals of the platinum group or their colloidal solutions.

Hydroquinine ethyl carbonate (*loc. cit.*) is obtained when quinine ethyl carbonate (10 parts), 20% sulphuric acid (14 parts), and 80 parts of water are shaken with 0·1 part of colloidal palladium in 10 parts of water in an atmosphere of hydrogen under pressure until no further absorption of hydrogen is observed ; ammonium hydroxide is added, and the product extracted with ether.

Acetylhydroquinine, large, colourless crystals, m. p. 100°, is prepared in a similar way from acetylquinine, and *p*-aminobenzoylhydroquinine (*loc. cit.*) is also described.

<div align="right">F. M. G. M.</div>

Preparation of Esters of Hydrogenised Cinchona Alkaloids. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 253357. Compare A., 1912, i, 1013, and preceding abstract).

—The following esters are of therapeutic value.

Hydrocinchonine ethyl carbonate, colourless, tasteless needles, m. p. 134°, is obtained when cinchonine ethyl carbonate (30 parts) dissolved in 160 parts of alcohol is shaken with 1 part of colloidal palladium in 60 parts of water until the absorption of hydrogen ceases.

Benzoylhydrocupreine, colourless crystals, m. p. 172°, is prepared from hydrocupreine.

Dibenzoylhydrocupreine, needles, has m. p. 147°, whilst *ethylhydrocupreine ethyl carbonate* is obtained from ethylhydrocupreine and ethyl chloroformate in benzene solution ; it is conveniently isolated in the form of its *salicylate,* colourless crystals, m. p. 138—142°.

<div align="right">F. M. G. M.</div>

Physostigmine [Eserine]. FRANZ EISSLER (*Biochem. Zeitsch.*, 1912, 46, 502).

—Eserine gives with diazotised sulphanilic acid in alkaline solution a red colour, which indicates the presence of a pyrrole ring.

This result is in accordance with the recent investigations of Salway (T., 1912, 101, 978).   S. B. S.

d-Lupanine. AUGUST BECKEL (*Arch. Pharm.*, 1912, 250, 691—710. Compare A., 1911, i, 743).—In continuation of previous work, the oxidation of *d*-lupanine by various agents has been investigated, and the products obtained are described.

Chromic acid in large excess oxidises lupanine to a substance containing two additional oxygen atoms, but this was produced in too small quantity to be isolated. Hydrogen peroxide gives rise to two products: the first of these gives an *aurichloride*, m. p. 214°, crystallising in needles, and the other an *aurichloride*, m. p. 188—189°, and *platinichloride*, m. p. 222—227°, crystallising in rosettes of needles. Analyses of these double salts indicate that both oxidation products have the formula $C_{15}H_{24}O_2N_2$. Potassium permanganate in presence of sodium carbonate oxidises lupanine to a *product*, $C_{15}H_{24}O_3N_2$, which was isolated as the *aurichloride*, m. p. 188—189°, and converted into the *platinichloride*, $B_2,H_2PtCl_6,2H_2O$, m. p. 219—221° (decomp.), crystallising in needles.

In the action of bromine on lupanine no fission occurs, as has been suggested by previous workers (Callsen, A., 1900, i, 186; Soldaini, A., 1905, i, 371). A perbromide of the alkaloid is first formed, and this on warming with alcohol may give rise to several different products, depending on the conditions observed. In the present series of experiments, three products melting at 228—236°, 190—210°, and 186—188° respectively were obtained. The first of these consists essentially of *ethoxylupanine dihydrobromide*, $C_{15}H_{23}ON_2 \cdot OEt,2HBr$, m. p. 227—228°, $[\alpha]_D^{15-23} -129\cdot4°$, which crystallises in colourless, slender needles from boiling alcohol, and is apparently the "substance, $C_8H_{15}ON,HBr$," described by previous workers. The specific rotation falls, slowly in the cold, more rapidly on warming, when this substance is dissolved in hydrobromic acid, but returns to its normal value when the solution is mixed with alcohol and evaporated to dryness. In presence of excess of alkali the alkaloid is dextrorotatory. The *dihydriodide*, m. p. 221—222°, forms colourless needles; the *dithiocyanate*, $C_{15}H_{23}ON_2 \cdot OEt,2HSCN,H_2O$, m. p. 172—174°, crystallises from water in colourless needles, and becomes anhydrous at 100°. The *aurichloride*, $(C_{15}H_{23}ON_2 \cdot OEt)_2,4HCl,3AuCl_3$, m. p. 145—150°, crystallises in small, yellow leaflets, and on warming in dilute hydrochloric acid gives *hydroxylupanine aurichloride*,
$$(C_{15}H_{23}ON_2 \cdot OH)_2,4HCl,3AuCl_3,$$
which sinters at 122—123°, and crystallises badly in leaflets. Ethoxylupanine does not readily reduce permanganate. Hydriodic acid converts it into a substance which was isolated as the methiodide; the latter resembles lupanine methiodide in rotation, crystalline form, and melting point, but on treatment with silver chloride and gold chloride yields an *aurichloride*, $(C_{15}H_{24}ON_2,MeCl,AuCl_3)_2,HAuCl_4$, m. p. 210°, crystallising in leaflets, whilst the aurichloride obtained in like manner from lupanine methiodide has the composition
$$C_{15}H_{24}ON_2,MeCl,AuCl_3,$$
and melts at 200—205°. The *platinichloride*, m. p. 224—226°,
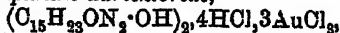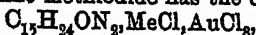
crystallises in slender, brown needles, and is also abnormal in composition.

The second oxidation product, m. p. 190—210°, contained some ethoxylupanine dihydrobromide, and after the removal of this formed a crystalline mass, m. p. 192—194°, which was probably a mixture of hydrobromides.

The third product, m. p. 186—188°, on recrystallisation from boiling alcohol gave what seems to be a mixture of ethoxylupanine dihydrobromide with either hydroxylupanine hydrobromide or lupanine dihydrobromide, whilst from the mother liquor d-*lupanine dihydrobromide*, $B,2HBr,H_2O$, m. p. 188—189°, $[a]_D + 45\cdot9°$, was isolated.

T. A. H.

Morphineglucoside. CARL MANNICH (*Annalen*, 1912, **394**, 223—228).—Morphine in $N/2$-sodium hydroxide is shaken for six hours with ethereal β-acetylbromoglucose. The ethereal solution is shaken with 1% hydrochloric acid The acid extract, by treatment with ammonia, yields *morphinetetra-acetylglucoside*,

$$C_{17}H_{18}O_3N\cdot C_6H_7O_5Ac_4,H_2O,$$
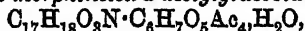
m. p. 154—156°, colourless needles (*hydrochloride*, m. p. about 220° [decomp.]). By hydrolysis with $N/2$-alcoholic potassium hydroxide, the substance yields *morphineglucoside*, $C_{17}H_{18}O_3N\cdot C_6H_{11}O_5,H_2O$, m. p. 183—193°, fine needles. The glucoside, which is more conveniently obtained by the interaction of morphine, $N/2$-sodium hydroxide, and acetylbromoglucose in aqueous acetone and hydrolysis of the product, does not reduce boiling Fehling's solution, and yields dextrose and morphine by hydrolysis with $N/2$-hydrochloric acid on the water-bath. C. S.

Alkaloids of Pareira Root. MAX SCHOLTZ (*Arch. Pharm.*, 1912, **250**, 684—691. Compare A., 1899, i, 92; 1907, i, 79; 1911, i, 913, and Faltis, A., 1912, i, 796).—A reply to Faltis (*loc. cit.*) criticising his results and suggesting, as the result of new analyses, that the bebeerines are better represented by the formula $C_{17}H_{19}O_3N$ than by those previously suggested by the author and by Faltis. T. A. H.

Protopine and Cryptopine. PETER W. DANCKWORTT (*Arch Pharm.*, 1912, **250**, 590—646).—A résumé of previous papers relating to the distribution of protopine in the natural orders, *Papaveraceae* and *Fumariaceae*, and its characters and chemistry is first given. It is then shown by analogy with other papaveraceous alkaloids that protopine probably contains an *iso*quinoline group, and evidence is brought forward for the view that it contains two methylenedioxy-groups and a carbonyl group, and that the nitrogen atom has a ·CH₃ group attached to it. On these and other grounds the annexed formula is assigned provisionally to the alkaloid.
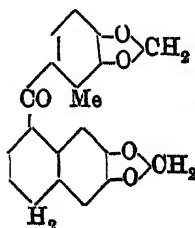
Dicentra (*Diclytra*) *spectabilis* tubers yielded 0·65% of crude alkaloid, chiefly protopine. The latter has the formula $C_{20}H_{19}O_5N$, and crystallises from a mixture of chloroform and alcohol

in colourless prisms or from ether in nodular masses : both forms melt at 207°, but the first gives with sulphuric acid a yellow coloration changing to blue, reddish-violet, and green, and with Fröhde's reagent a yellowish-olive colour changing to dirty violet, green, blue, and finally green ; the second form, on the contrary, with sulphuric acid gives a deep yellow, passing into green, dirty reddish-brown, and finally green, whilst with Fröhde's reagent it yields a yellowish-olive solution which becomes violet and finally green.

Protopine contains no hydroxyl groups or methoxyl groups, but gives Gaebel's test for dioxymethylene (A., 1910, i, 501), and the presence of the latter is confirmed by the fact that protopine, when heated under pressure with dilute sulphuric acid, yields a product giving the colour reactions of a catechol derivative. No direct evidence of the presence of a carbonyl group could be obtained. The occurrence of a $:NCH_3$ group was proved by Herzig and Meyer's method. The alkaloid is not reduced by aqueous colloidal platinum, but sodium amalgam in dilute acid converts it into *hydroprotopine*, $C_{20}H_{21}O_5N,\frac{1}{2}EtOH$, m. p. 120° (approx.) or 151—152° (dry), which crystallises from a mixture of ether and alcohol, becomes anhydrous at 100°, is easily soluble in chloroform or ethyl acetate, sparingly in alcohol and slightly in ether; the *hydrochloride* crystallises from alcohol in needles and from water in plates. On treatment with benzoyl chloride hydroprotopine is apparently first benzoylated and then partly converted by loss of H_2O into a *quaternary base*, $C_{20}H_{19}O_4N$, which has not been obtained free from the benzoylated product ; it yields a *hydrochloride*, $C_{20}H_{19}O_4N,HCl,5H_2O$, m. p. 275° (approx. decomp.), which is crystalline and from which an *aurichloride*, $B,HAuCl_4$, crystallising in reddish-brown needles is obtainable ; this hydrochloride on heating with sodium hydroxide in alcohol is converted into an isomeric *tertiary anhydro-base*, $C_{20}H_{19}O_4N$, m. p. 145°, crystallising in long needles. Both the quaternary and the tertiary anhydro-bases can be prepared in other ways from protopine and hydroprotopine ; it is believed that this series of changes from protopine to the tertiary anhydro-base takes place in the following

way : $\cdot NMe\cdot \overset{\cdot}{C}H\cdot CO\cdot \longrightarrow \cdot NMe\cdot \overset{\cdot}{C}H\cdot CH(OH)\cdot \longrightarrow$

$$\cdot (HCl)NMe\cdot CH\cdot CH(OBz)\cdot \longrightarrow$$

$$\cdot ClNMe\dot{:}C\cdot CH_2\cdot \rightleftharpoons \cdot (HO)NMe\dot{:}CH\cdot CH_2\cdot \rightleftharpoons \cdot NMe\cdot C\dot{:}CH\cdot,$$
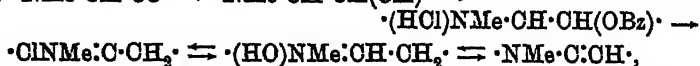
the compound represented by the fourth formula being the "hydrochloride" of the quaternary base, and that by the sixth formula being the tertiary anhydro-base.

Methyl iodide converts protopine into the methiodide, whilst methyl sulphate transforms it into *methylprotopine methosulphate*, $C_{20}H_{19}O_5NMe\cdot SO_4Me$, which crystallises from dilute alcohol : either of these substances on heating with alkalis yields *protopinemethine*, $C_{20}H_{18}O_5NMe$, m. p. 136—137°, crystallising in pearly leaflets, which in turn furnishes a crystalline *methiodide*; this on heating with alkali hydroxides in methyl alcohol yields trimethylamine and an amorphous product.

The tertiary anhydro-base also yields a crystalline *methiodide*, m. p. 230°, and a crystalline *methine* base, m. p. 112°, which fluoresces

in ether solutions and gives a bromine additive product. The *methine-methiodide*, rosettes of needles, is not decomposed on heating with alkalis in methyl alcohol, but on treating the methine base with methyl sulphate and heating the product with sodium hydroxide in methyl alcohol an amine is evolved and a resinous vinyl derivative is formed.

Oxidation experiments with protopine and its derivatives did not afford useful results, except in the case of protopinemethine, which on treatment with potassium permanganate in acetone solution yielded a basic substance and hydrastic acid (4 : 5-methylenedioxyphthalic acid).

Cryptopine resembles protopine in its solubilities, and in physiological action, and like it contains no hydroxyl group and gives no oxime. Cryptopine contains a methylenedioxy-group, and two methoxyl groups. On reduction with sodium amalgam in dilute sulphuric acid it yields *hydrocryptopine*, m. p. 182—183°, which crystallises from ether and on treatment with benzoyl chloride gives the *hydrochloride* of a *quaternary base*. In view of this it seems likely that cryptopine differs from protopine only in containing two methoxyl groups in place of one methylenedioxy-group, but it is not clear which of the two methylenedioxy-groups of protopine is thus replaced (compare Pictet and Kramers, A., 1910, i, 502, and Brown and Perkin, P., 1891, 7, 161).   T. A. H.

Preparation of Acyl Derivatives of Theobromine   KNOLL & Co. (D.R.-P. 252641).—*Acetyltheobromine*, colourless, odourless needles with a bitter taste and m. p. 165°, is obtained by the action of acetyl chloride on a solution of sodium theobromine in chloroform or xylene.

Benzoyltheobromine forms colourless, odourless, tasteless needles, m. p. 206° (about), and is most satisfactorily prepared from silver theobromine and benzoyl chloride in toluene solution.

These compounds are of therapeutic value, and analysis indicates that they are monoacyl derivatives.   F. M. G. M.

The Chemical Constitution of Sparteine. CHARLES MOUREU and AMAND VALEUR (*Ann. Chim. Phys.*, 1912, [viii], 27, 245—391).— A résumé of work already published (compare A., 1903, i, 717 ; 1904, i, 187 ; 1905, i, 608, 609, 659, 716 ; 1908, i, 43, 44, 103, 206, 563 ; 1911, i, 319, 562 ; 1912, i, 210, 296).   W. G.

Some New Sparteine Salts. LOUIS CORBIEZ (*Chem. Zentr.*, 1912, ii, 1566 ; from *Bull. Sci. Pharmacol.*, 19, 468—480).—The following salts are described : *Basic hydrobromide*, B,HBr [$B = C_{15}H_{26}N_2$], from the basic sulphate and barium bromide, prismatic crystals, m. p. 236°, $[a]_D - 16°6'$; *di-iodide*, B,2HI + H_2O, m. p. (anhydrous) 225°, $[a]_D - 16°2'$; *normal chlorate*, B,2HClO$_3$, colourless cubes, explodes at 147°, $[a]_D - 23°12'$; *basic chlorate*, B,HClO$_3$, colourless prisms, explodes at 200—205°, $[a]_D - 16°3'$; *normal perchlorate*,

$$B,2HClO_4 + 2H_2O,$$
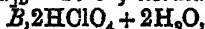
prisms, m. p. 78°, anhydrous, 265°, explodes over 300°, $[a]_D - 17°30'$;

basic perchlorate, $B,HClO_4$, m. p. 171°, $[a]_D$ in methyl alcohol $-17°6'$, in acetone $-16°3'$; *dichromate,* $B,H_2Cr_2O_7$, orange-yellow prisms, decomposes at 128—129°; *normal salicylate,* $B,2C_7H_6O_3 + H_2O$, pale pink prisms, m. p. 78°, $[a]_D -8°42'$.　　　　　　　　　　J. C. W.

The Constitution of Sparteine Periodide and Sparteine Perbromide. Louis Corriez (*Chem. Zentr.*, 1912, ii, 1826; from *Bull. Sci. Pharmacol.*, 1912, 19, 533—540).—The formation of sparteine periodide by the action of 12% hydrogen peroxide on sparteine di-iodide may be expressed thus: $2C_{15}H_{26}N_2 2HI + O = 2C_{15}H_{26}N_2.HI + I_2 + H_2O$; $C_{15}H_{26}N_2.HI + I_2 = C_{15}H_{26}N_2.HI,I_2$. As it would follow from the latter equation, the periodide also results when sparteine mono- or di-iodide is treated with iodine. *Sparteine perbromide,*

$$C_{15}H_{26}N_2,2HBr,Br_2 + H_2O,$$

by the action of bromine on sparteine, both dissolved in fuming hydrobromic acid, forms yellow crystals, m. p. 193°. The formation of this perbromide will show the presence of sparteine in a dilution of 1 : 10,000.　　　　　　　　　　J. C. W.

New α-Methylsparteinium Salts. Louis Corriez (*Chem. Zentr.*, 1912, ii, 1826; from *Bull. Sci. Pharmacol.*, 1912, 19, 527—532).— Starting from α-methylsparteinium hydroxide, which is obtained in aqueous solution by the action of moist silver oxide on Moureu's α-sparteine methiodide (A., 1905, i, 608), the following salts have been prepared: *Hydrochloride* of *α-sparteine methochloride,*

$$C_{15}H_{26}N_2MeCl,HCl,3H_2O,$$
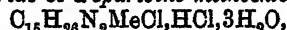
transparent, hygroscopic crystals, m. p. 194°, $[a]_D -23°9'$; *hydrobromide* of *α-sparteine methobromide,* $C_{15}H_{26}N_2MeBr,HBr,2H_2O$, m. p. 216°, $[a]_D -19°2'$; *α-methylsparteinium dichromate,*

$$C_{15}H_{26}N_2Me\cdot Cr_2O_7H,H_2O,$$
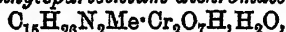
orange-yellow needles, decomposes at 120°; *α-methylsparteinium perchlorate,* $C_{15}H_{26}N_2Me\cdot ClO_4$, transparent needles, decomposes at 230°; *α-methylsparteinium picrate,* $C_{15}H_{26}N_2Me\cdot C_6H_2O_7N_3$, yellow needles, m. p. 218°.　　　　　　　　　　J. C. W.

Pyrrolidonecarboxylic Acid and Polypeptides Derived from It. Emil Abderhalden and Erich Wurm (*Zeitsch. physiol. Chem.*, 1912, 82, 160—166).—Pyrrolidonecarboxyl chloride interacts with cholesterol in chloroform solution in the absence of moisture, forming *cholesteryl pyrrolidonecarboxylate,* $C_{26}H_{43}\cdot O\cdot CO\cdot CH{<}^{CH_2\cdot CH_2}_{NH-CO}$. This crystallises in colourless, matted needles, which sinter at 199—203°, m. p. 205°.

dl-*Pyrrolidonecarboxyl-d-alanine ester* crystallises in rosettes of needles, m. p. 125·5° (corr.), $[a]_D^{20} -46·42°$.

dl-*Pyrrolidonecarboxyl-dl-leucine ester* separates in prisms, m. p. 115—117° (corr.).　　　　　　　　　　E. F. A.

Chalkones and Hydrochalkones. III. Guido Bargellini and E. Martegiani (*Gazzetta*, 1912, 42, ii, 427—432. Compare this vol., i, 59).—The authors have applied the mode of reduction previously

described to compounds analogous to chalkones, but containing pyrrole and furan rings, instead of benzene rings. In all cases only two atoms of hydrogen were added, and the rings were not attacked; the experiments were conducted in alcoholic solution (compare Willstätter and Hatt, A., 1912, i, 545).

2-Cinnamoylpyrrole (compare Ciamician and Dennstedt, A., 1885, 378) is conveniently prepared by keeping a mixture of 2-acetylpyrrole and benzaldehyde in the presence of potassium hydroxide in aqueous-alcoholic solution. The *dihydro*-derivative, $C_{13}H_{13}ON$, forms colourless needles, m. p. $70-71°$. It dissolves in concentrated sulphuric acid, giving a colourless solution.

2-mp-*Methylenedioxycinnamoylpyrrole*, $C_{14}H_{11}O_3N$, is obtained by keeping 2-acetylpyrrole and piperonaldehyde in the presence of potassium hydroxide in aqueous-alcoholic solution. It dissolves in concentrated sulphuric acid, giving an intense red coloration. On reduction it yields a *dihydro*-derivative, $C_{14}H_{13}O_3N$, which forms colourless needles, m. p. $84-85°$, and dissolves in concentrated sulphuric acid, giving a colourless solution.

Furfurylidenepaenol (compare Courant and von Kostanecki, A., 1907, i, 75) gives a *dihydro*-derivative, $C_{14}H_{14}O_4$, which forms colourless needles, m. p. $72-73°$.

2-*Furfurylideneacetylpyrrole*, $C_{11}H_9O_2N$, crystallises in yellow needles, m. p. $130-131°$; it dissolves in concentrated sulphuric acid, giving an intense red coloration. Its *dihydro*-derivative, $C_{11}H_{11}O_2N$, crystallises in colourless needles, m. p. $70-71°$.   R. V. S.

Preparation of 2-Indolecarboxylic Acid and 2:3-Dihydroxy-quinoline from Oxal-*o*-toluidic Acid. Indole Syntheses. II. WALTER MADELUNG (*Ber.*, 1912, **45**, 3521—3527. Compare A., 1912, i, 499).—The synthesis of indole compounds recently described (*loc. cit.*) fails with the application of formyl derivatives, and so the direct synthesis of indole itself in this way fails. By the use of oxal-*o*-toluidic acid, however, the action proceeds in the normal manner with the formation of the expected indolecarboxylic acid, which by careful distillation can be converted into indole (Weissgerber, A., 1911, i, 155).

Oxal-*o*-toluidic acid is conveniently obtained by heating a mixture of equal quantities of *o*-toluidine and anhydrous oxalic acid for an hour at a temperature not exceeding $130°$; the concentrated solution of the toluidine salt of the acid on treatment with the necessary quantity of dilute sulphuric acid gives a thick deposit of the free acid. On evaporating the solvent from an alcoholic solution of sodium ethoxide and potassium oxal-*o*-toluidate and raising the temperature of the resultant intimate mixture to $340-350°$, reaction takes place with the formation of two products, one of which can be easily dissolved out with benzene. This substance by m. p. $199-202°$, and by its yielding indole on heating was evidently indolecarboxylic acid.

The sparingly soluble constituent, prisms, m. p. $257-258°$, gives a *diacetyl* derivative, needles, m. p. $211°$, and produces with ferric chloride a bluish-green coloration; it is inappreciably attacked by phosphorus pentachloride even at $140°$, the only result being a minute

quantity of a *substance*, m. p. 70—90°. It is highly probable that this second constituent of the mixture produced in the original synthesis is 2 : 3-*dihydroxyquinoline*. This decision is at variance with tho published results of Friedländer and Weinberg (A., 1883, 351), who ascribe a considerably higher m. p. and no ferric chloride coloration. A repetition of Friedländer and Weinberg's method of preparation, namely, fusion of 3-chloro-2-hydroxyquinoline with potassium hydroxide, showed that under certain conditions the dihydroxyquinoline, m. p. above 300°, of these investigators becomes a subsidiary product, whilst a by-product mentioned by them becomes the main resultant substance, identical with the author's dihydroxyquinoline. The correctness of this view, that the earlier description of dihydroxyquinoline is a mistake, is confirmed by the action of phosphorus pentachloride, which converts the substance (m. p. above 300°) into a compound which sinters at 102°, decomposes at a higher temperature, and is quite distinct from 2 : 3-dichloroquinoline.   D. F. T.

Preparation of Derivatives of 2-Phenylquinoline-4-carboxylic Acid and its Homologues. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 252643).—2-Phenylquinoline-4-carboxylic acid and its homologues, although of therapeutic value, have the disadvantage of a bitter taste; this drawback is absent in the amides which have now been prepared.

The *chloride* of 2-phenylquinoline-4-carboxylic acid is a yellow powder, m. p. 230°, and the *amide*, glistening, colourless, hair-like needles, m. p. 195°; whilst the *amide* of 2-phenyl-6-methylquinoline-4-carboxylic acid forms glistening needles, m. p. 257°.

F. M. G. M.

Salts of Acridine, Pyridine, and Quinoline. LEE H. CONE (*J. Amer. Chem. Soc.*, 1912, **34**, 1695—1706).—The object of this work was to study the analogy between the derivatives of the triphenylcarbinols and xanthenols, on the one hand, and those of the acridols on the other, and to show that this analogy extends to the salts of pyridine and quinoline. It has been found that the haloids of phenylacridol, pyridine, and quinoline react with silver to form silver haloids and unsaturated compounds, similar to triphenylmethyl, which readily absorb oxygen. The ammonium salts, such as phenylbenzyldimethylammonium chloride and tetramethylammonium iodide, do not react in this way. The conclusion is therefore drawn that the salts of acridine, pyridine, and quinoline are probably quinocarbonium salts and not ammonium salts, as has been generally assumed.

When diphenylacridol chloride (Gomberg and Cone, A., 1910, i, 59) is suspended in nitrobenzene and treated with molecular silver, a double *silver* salt, $C_{25}H_{18}NCl,AgCl$, is produced, together with an unsaturated compound which absorbs oxygen to form a peroxide, thus: (1) $C_{25}H_{18}NCl + Ag = C_{25}H_{18}N- + AgCl$; (2) $C_{25}H_{18}NCl + AgCl = C_{25}H_{18}NCl,AgCl$; (3) $2C_{25}H_{18}N- + O_2 = (C_{25}H_{18}N)_2O_2$.

When 5-*phenyl*-10-*methylacridol chloride hydrochloride*,

$$NMe\underset{C_6H_4\underline{\quad\quad}}{\overset{C_6H_4(Cl,HCl)}{<}}\hspace{-0.3em}>CPh,$$
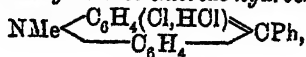
is heated at 90—100° and a current of air passed through it, it is converted into the *chloride*, $NMe{<}^{C_6H_4Cl}_{C_6H_4}{>}CPh$, which, on being treated with molecular silver, yields a double *silver* salt,

$$C_{20}H_{16}NCl,AgCl,$$
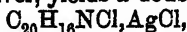
and an unsaturated compound which absorbs oxygen.

If pyridine methyl iodide is shaken with nitrobenzene and excess of silver, a similar reaction occurs with formation of a double iodide and an unsaturated compound which absorbs oxygen. Quinoline methiodide behaves in the same way.   E. G.

Acridine Derivatives. II. Analogue of *apo*Safranone in the Acridine Series. FRIEDRICH KEHRMANN and ZD. MATUSINSKY (*Ber.*, 1912, **45**, 3498—3505).—2-Hydroxy-5-phenylacridine is best obtained by heating, without stirring, an intimate mixture of *m*-hydroxy-diphenylamine, benzoic acid, and zinc chloride at 180—200°, and finally at 210°, for half an hour at each temperature; a crystalline by-product is also obtained, the removal of which presents some difficulty. The hydroxyphenylacridine crystallises from hot saturated solutions in straw-yellow needles, m. p. 264°, and at the ordinary temperature in brick-red prisms, m. p. about 135°, changing to the yellow modification. On the contrary, the yellow form changes to the red by long keeping at the ordinary temperature. The suggestion is offered that the two modifications have an ortho- and a para-quinonoid constitution respectively:

$$C_6H_4{<}^{CPh}_{-N}{>}C_6H_3 \cdot OH \text{ and } C_6H_4{<}^{CPh}_{NH}{>}C_6H_3 \vdots O.$$
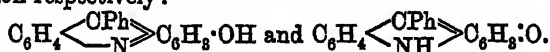
2-Acetoxy-5-phenylacridine, m. p. 151°, pale-yellow leaflets, reacts with methyl sulphate in nitrobenzene at 140—150° to form *2-acetoxy-5-phenyl-10-methylacridinium methosulphate*,

$$CPh{<}^{C_6H_4-}_{C_6H_3(OAc)}{>}NMe \cdot SO_4Me,$$
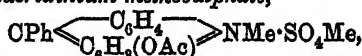
citron-yellow needles, from which a *chloride*, *bromide*, *iodide*, and *platinichloride*, yellow to orange-red, crystalline salts, can be prepared.
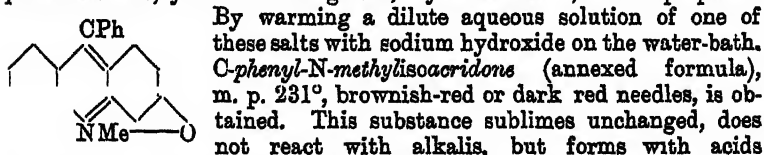
By warming a dilute aqueous solution of one of these salts with sodium hydroxide on the water-bath. C-*phenyl*-N-*methyl*iso*acridone* (annexed formula), m. p. 231°, brownish-red or dark red needles, is obtained. This substance sublimes unchanged, does not react with alkalis, but forms with acids crystalline, red and yellow salts which are completely hydrolysed by water. It yields salts of the preceding acetoxyphenylmethylacridinium base by prolonged keeping with acetic anhydride and treatment of the resulting solution with metallic salts, and is converted by methyl sulphate in nitrobenzene at 150° into 2-*methoxy-5-phenyl-10-methylacridinium methosulphate*, citron-yellow needles, from which the corresponding *chloride*, *iodide*, *platinichloride*, and *dichromate* have been prepared.   C. S.

Action of Phthalic Anhydride on Some Pyrrole Derivatives. HANS FISCHER and FR. KROLLPFEIFFER (*Zeitsch. physiol. Chem.*, 1912, **82**, 266—272).—The trisubstituted pyrroles are at

present characterised as picrates or as the azo-dyes formed with diazobenzenesulphonic acid. They also form characteristic crystalline phthalides when heated with phthalic anhydride and acetic acid in sealed tubes at 180—190°.

3-*Acetyl-2 : 4-dimethylpyrrolephthalide,*

$$C_6H_4 {\scriptstyle <} {\overset{\textstyle CO \cdot C : OMe}{\underset{\textstyle CO \cdot N \cdot CMe}{}}} {\scriptstyle >} C \cdot COMe,$$
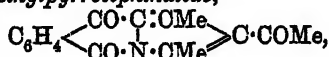
crystallises in faintly yellow-coloured needles, m. p. 183°. On heating with potassium hydroxide it is converted into the corresponding *acid*, which crystallises in slender, colourless needles, m. p. 176—178°.

Cryptopyrrolephthalide separates in brownish-yellow needles, m. p. 169°; the corresponding acid has m. p. 195° (decomp.).

Phonopyrrolecarboxylic acid phthalide forms faintly yellow-coloured needles, m. p. 225—226°; it can be prepared easily from syrupy phonopyrrolecarboxylic acid.

Haemopyrrolephthalide forms yellow prisms, m. p. 116°.

Tetramethylpyrrole and phthalic anhydride yield a *trimethylpyrrolephthalide*, crystallising in stunted, yellow prisms, m. p. 205°. The *acid* obtained on heating with potassium hydroxide has m. p. 204° (decomp.).   E. F. A.

The Methylation of Gallocyanin, Pyrogallin, and Azurin. FRIEDRICH KEHRMANN and A. BEYER (*Ber.*, 1912, **45**, 3338—3345).— The preparation of oxonium salts analogous to those obtained from resorufin (Kehrmann and Vogt, A., 1910, i, 409) offers in the case of the above substances considerably more difficulty.

The starting substances, gallocyanin, its methyl ester, pyrogallin (m. p. 240—241°), and azurin were first carefully purified and their properties re-examined.

Gallocyanin, on methylation in sodium hydroxide solution with methyl sulphate, gave the phenolic *ether*, $O {\scriptstyle <} {\overset{\textstyle C_6H(OMe)(CO_2H)}{\underset{\textstyle O \longrightarrow C_6H_8(NMe_2)}{}}} {\scriptstyle >} N,$ deep blue powder, m. p. 203—204°, which forms salts with acids and bases; the solution of this substance in fuming sulphuric acid when diluted changes colour from red to blue, and again to red, indicative of the existence of tri-, di-, and mono-acid salts. Simultaneously with the above ether there is obtained *dimethylgallocyanin,*

$$O {\scriptstyle <} {\overset{\textstyle C_6H(OMe)(CO_2Me)}{\underset{\textstyle O \cdot C_6H_8(NMe_2)}{}}} {\scriptstyle >} N,$$
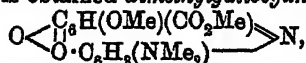
which is better obtained, however, by the action of methyl sulphate on the methyl ester of gallocyanin; it forms prisms with a bronze lustre, m. p. 197°, is insoluble in alkalis, but with acids gives crystalline salts; the solution in fuming sulphuric acid on dilution gives the same series of colour changes as the phenolic ether; *platinichloride*, crystalline.

Methyl sulphate acts on an alkaline solution of pyrogallin, giving a phenolic *ether*, $O {\scriptstyle <} {\overset{\textstyle C_6H_2(OMe) \longrightarrow}{\underset{\textstyle O \cdot C_6H_8(NMe_2)}{}}} {\scriptstyle >} N,$ prisms with a green lustre, m. p. 199—200°. The solution in fuming sulphuric acid shows the usual colour changes on dilution.

Azurin can be methylated by heating with methyl alcohol containing a little hydrochloric acid, forming the *ester*, $O<{C_{10}H_2(CO_2Me)= \atop O \cdot C_6H_3(NMe_2)}>N$, prisms with a metallic lustre, m. p. 190°; the solution in concentrated mineral acid changes from a blue to a red colour on dilution.

<div align="right">D. F. T.</div>

Preparation of Anthrapyridonecarboxylic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 250885).—When the compound, $C_6H_4<{CO \atop CO}>C_6H_3 \cdot NH \cdot CO \cdot CH_2 \cdot CO_2Et$ obtained by heating together molecular proportions of ethylmalonyl
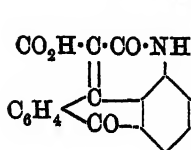
CO₂H·C·CO·NH
‖
$C_6H_4<{CO \atop CO-}$

chloride and α-aminoanthraquinone at 200° is boiled with aqueous sodium hydroxide it yields *anthrapyridonecarboxylic acid*, $C_{17}H_9O_4N$ (annexed formula); this compound exhibits a yellow fluorescence when dissolved in concentrated sulphuric acid.

The analogous *compound*, $C_{17}H_{10}O_4N_2$, prepared from 1 : 4-diamino-anthraquinone is a red powder; and the *compound* from 4-chloro-1-aminoanthraquinone an orange-yellow powder. F. M. G. M.

Preparation of Anthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252839).—The condensation of aldehydes with *o*-diaminoanthraquinones has been recorded; this action is now found to take place with 1-amino-2-hydroxyanthra-quinone or with 1-aminoanthraquinone-2-thiol, yielding compounds of the general formulæ :

$$A<{NH_2 \atop OH} \rightarrow A<{N \atop O}>CR. \qquad A<{NH_2 \atop SH} \rightarrow A<{N \atop S}>CR.$$
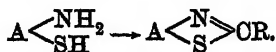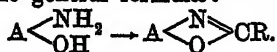
The following *compounds* are described: from benzaldehyde with (1) 1-amino-2 : 4-dihydroxyanthraquinone, an orange, crystalline powder; (2) with 2 : 4-diamino-1-hydroxyanthraquinone, brown crystals; (3) with 3-amino-1 : 2-dihydroxyanthraquinone, orange needles; (4) with 1 : 5-diamino-2:4:6:8-tetrahydroxyanthraquinone; (5) with 1-aminoanthraquinone-2-thiol; from 1-amino-2 : 4-dihydroxy-anthraquinone with paraformaldehyde, whilst the *anthra*-1 : 2-*oxazole* rom 1-amino-2-hydroxyanthraquinone forms yellow crystals.

<div align="right">F. M. G. M.</div>

1-Amino-2-methylanthraquinone-α-quinolines. ALFRED SCHAAB-SCHMIDT and ALEX. STAHLSCHMIDT (*Ber.*, 1912, 45, 3452—3456).—These substances have been prepared in order to ascertain what influence the presence of a quinoline nucleus has on the colour of the already intensely coloured 1-aminoanthraquinone. The dinitration of 2-methylanthra-quinone by concentrated nitric and sulphuric acids yields a mixture of 1 : 5-*dinitro-2-methylanthraquinone*, m. p. 251—252°, and 1 : 8-*dinitro-2-methylanthraquinone*, m. p. 189—190°, which is separated by the sparing solubility of the former in boiling glacial acetic acid. The two substances, the orientation of the nitro-groups in which is assumed from analogy to the course of the nitration of anthraquinone,

are reduced by alkaline sodium sulphide to 1 : 5-*diamino-2-methyl-anthraquinone*, m. p. 201—202°, red needles, and 1 : 8 *diamino-2-methylanthraquinone*, m. p. 206—208°, brownish-red needles, from which the quinolines are obtained by the Skraup method. 1-*Amino-2 methyl-anthraquinone-5-quinoline* (formula I), m. p. 206—207, reddish-brown
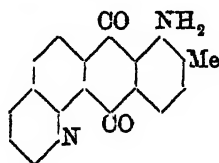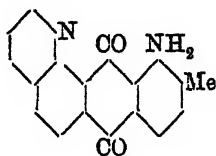
(I.)   (II.)

needles, dissolves in concentrated sulphuric acid with a brownish-yellow colour changing to blue by dilution with water. 1-*Amino-2-methylanthra-quinone-8 quinoline* (formula II), m. p. 100°, reddish-brown crystals, forms violet solutions in dilute mineral acids.   C. S.

The Purification and Separation of Anthraquinoneacridones from By-products. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 253090).—*Bromoanthraquinoneacridone*, a yellowish-red powder (prepared from anthraquinoneacridone), has m. p. above 300°, and is conveniently purified by isolation in the form of its *sulphate*, whilst the action of sulphuryl chloride on anthraquinoneacridone furnishes a mixture of two isomeric *chloroanthraquinoneacridones*.   F. M. G. M.

[Preparation of 4:4'-Diamino-2:2'-dimethyldiphenyl-methane.] FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 252916).—*4 : 4'-Diaminodiphenylmethane* prepared from *m*-toluidine crystallises from hot water in colourless needles, m. p. 123°; the solution of its hydrochloride gives a violet coloration with ferric chloride, and when fully diazotised and combined with *a*-naphthol-5-sulphonic acid (2 mols.) furnishes a brownish-red azo-colouring matter. F. M. G. M.

Preparation of Aminobenzoyl Derivatives of Aminobenzoyl-7-amino-1-naphthol-3-sulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252159).—The tinctorial properties of the compounds obtained by the action of nitrobenzoyl haloids on aminobenzoyl-7-amino-1-naphthol-3-sulphonic acid and subsequent reduction have been recorded; it is now found that these compounds can be obtained by the combination of an aminobenzoic acid with a nitrobenzoyl haloid, followed by condensation with 7-amino-1-naph-thol-3-sulphonic acid and subsequent reduction.   F. M. G. M.

Action of Hydroxylamine and of Phenylhydrazine on Urethanobenzylacetylacetone and on Ethyl Urethanobenzyl-acetoacetate. G. BIANCHI (*Gazzetta*, 1912, 42, ii, 496—512. Compare A., 1912, i, 542; Bianchi and Schiff, A., 1911, i, 977).—By the action of hydroxylamine on ethyl urethanobenzylacetoacetate, a stable

compound, $C_{16}H_{22}O_5N_2$, is obtained, which crystallises in colourless needles, m. p. 185° (sintering a few degrees previously). This compound is the normal *oxime*,

$$OH \cdot N\hspace{-0.3em}:\hspace{-0.3em}CMe \cdot CH(CO_2Et) \cdot CHPh \cdot NH \cdot CO_2Et.$$

The action of hydroxylamine on urethanobenzylacetylacetone yields two compounds. One, which forms heavy, prismatic crystals, m. p. 175° (decomp.), has the composition $C_{15}H_{20}O_4N_2$, and is the *monoxime*, $OH \cdot N\hspace{-0.3em}:\hspace{-0.3em}CMe \cdot CH(COMe) \cdot CHPh \cdot NH \cdot CO_2Et$; it is unstable and is obtained with difficulty. The other compound forms large, prismatic crystals, m. p. 94—95°; it is readily obtained and very stable; it has the composition $C_{15}H_{18}O_3N_2$ required by 4-*urethano-benzyl*-2 : 5-*dimethyl*isooxazole,

$$O \big\langle {\substack{CMe\hspace{-0.2em}:\hspace{-0.2em}C \cdot CHPh \cdot NH \cdot CO_2Et \\ N =\!\!= CMe}}$$

. The oxime readily changes into the *iso*oxazole derivative.

[With MANLIO ROCCHI.]—The action of phenylhydrazine on urethanobenzylacetylacetone and on ethyl urethanobenzylacetoacetate yields in each case the normal monophenylhydrazone. *Urethano-benzylacetylacetonephenylhydrazone*, $C_{21}H_{25}O_3N_3$, crystallises in groups of needles, m. p. 149—150° (decomp.). *Ethyl urethanobenzylaceto-acetatephenylhydrazone*, $C_{22}H_{27}O_4N_3$, crystallises in groups of needles, m. p. 136—137°. R. V. S.

Benzoylation of Aminourazole. ROBERT STOLLÉ and K. KRAUCH (*Ber.*, 1912, **45**, 3307—3311).—By the action of benzoyl chloride on aminourazole in presence of pyridine there are obtained a dibenzoylaminourazole, $C_2H_2O_2N_4(COPh)_2$, a tribenzoylaminourazole, and what was considered to be a tetrabenzoyl derivative. The last did not give aminourazole on hydrolysis, yielding instead a dibenzoyl derivative which proved to be identical with the benzoylhydrazi-carbonyl, $COPh \cdot N \big\langle {\substack{NH \\ CO}}$, obtained by Diels and Wagner (A., 1912, i, 511; compare Diels and Okada, *ibid.*, 918) by the action of alkali on chlorobenzoylcarbamide. The supposed tetrabenzoyl derivative is, therefore, *dibenzoylhydrazicarbonyl*, for which the symmetrical formula $CO \big\langle {\substack{N \cdot COPh \\ N \cdot COPh}}$ is considered most probable.
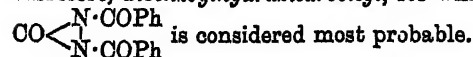
Dibenzoylaminourazole crystallises in needles, m. p. 201°, and yields aminourazole on hydrolysis.

Tribenzoylaminourazole forms tiny needles, m. p. 234°.

Dibenzoylhydrazicarbonyl has m. p. 130°. With sodium ethoxide, ethyl dibenzhydrazidoformate, m. p. 130° (Stollé and Benrath, A., 1904, i, 935), is obtained. On heating the carbonyl at 280°, 2:5-di-phenyl-1 : 3 : 4-oxadiazole is formed. E. F. A.

Constitution of the Compound from Benzoyl Chloro-carbamide and Alkali. PETER J. SCHESTAKOV (*Ber.*, 1912, **45**, 3273—3274. Compare Diels and Okada, A., 1912, i, 918; Diels and Wagner, A., 1912, i, 511).—A claim for priority. Schestakov, Kind,

and Lebedev (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 330) have prepared the compound described as benzoyl hydrazicarbonyl,

$$COPh \cdot N {<}^{NH}_{CO},$$
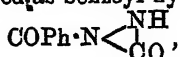
by Diels and Okada, and ascribe to it the formula $COPh \cdot N{<}^{N}_{C \cdot OH}.$

E. F. A.

Preparation and Properties of 5-Aminoquinoline-6 carboxylic Acid and Certain Related Compounds. MARSTON T. BOGERT and HARRY LINN FISHER (*J. Amer. Chem. Soc.*, 1912, **34**, 1569—1576).—This investigation was undertaken with the object of preparing an aminocarboxylic acid of the anthranilic type from which substances belonging to new heterocyclic systems might be obtained.

A method is described for the preparation of 5-nitro-6-methylquinoline (Noelting and Trautmann, A., 1891, 325). 5-Amino-6-methylquinoline has m. p. 135° (corr.); attempts to oxidise this compound to 5-aminoquinoline-6-carboxylic acid were not successful.

5-*Aminoquinoline*-6-*carboxylic acid*, $NH_2 \cdot C_9NH_5 \cdot CO_2H$, m. p. 218·5° (decomp.), obtained in 30% yield by boiling 5-nitro-6-methylquinoline with alcoholic potassium hydroxide, crystallises in red nodules; it yields brown, amorphous precipitates with barium chloride, calcium chloride, cadmium iodide, copper sulphate, indium chloride, and mercuric chloride, and green precipitates with nickel chloride and silver nitrate. The *hydrochloride* has m. p. 264·7°. The *methyl* ester crystallises in bright red needles with $2H_2O$; the anhydrous form, m. p. 245° (corr.), is an amorphous, scarlet powder. 5-*Acetylamino*-6-*quinolinecarboxylic acid*, m. p. 237° (corr., decomp.), obtained by the action of acetic anhydride on the acid, forms slender, yellow needles; by prolonged

heating with acetic anhydride it is converted into the *lactam*, $C_9H_5{<}^{CO}_{NAc}$

or $C_9H_5{<}^{CO \cdot O}_{N=CMe}$, m. p. 190° (uncorr.), which crystallises in nearly colourless needles, and reacts with primary amines to form naphtha*iso*triazines (this vol., i, 106). 5-*Benzylideneaminoquinoline*-6-*carboxylic acid*, $CHPh:N \cdot C_9NH_5 \cdot CO_2H$, m. p. 221·4° (corr., decomp.), forms rosettes of needles. 5-*Hydroxyquinoline*-6-*carboxylic acid*, m. p. 211·7° (corr., decomp.), is obtained as a dark green precipitate by the action of nitrous acid on the hydrochloride of the amino-acid, and crystallises in rosettes of brown needles; it yields green, amorphous precipitates with barium chloride, zinc chloride, cadmium iodide, copper sulphate, mercuric chloride, and silver nitrate.

E. G.

Preparation of Condensation Products from 1-Chloro-2:4-dinitrobenzene with the Leucoindophenols derived from Carbazole. LEOPOLD CASSELLA & Co. (D.R.-P. 252642).—Compounds having the annexed general formula, where R is hydrogen or alkyl, are obtained by the action of 1-chloro-2:4-dinitrobenzene on the leucoindophenols prepared from *p*-nitrosophenol with carbazoles. The *compounds* thus obtained
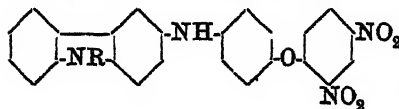
from the indophenols of carbazole with p-nitrosophenol (glistening, coppery leaflets, m. p. 190°) and from N-ethylcarbazole with p-nitrosophenol (small, reddish-brown needles, m. p. 223°) are described.

<div style="text-align:right">F. M. G.</div>

Constitution of isoQuinoline Red. II. EDUARD VONGERICHTEN and W. HOMANN (*Ber.*, 1912, **45**, 3446—3452. Compare A., 1910, i, 201).—The basic substance, $C_{19}H_{12}ON_2$, obtained together with benzaldehyde or benzoic acid by the oxidation of *iso*quinoline red by potassium dichromate and dilute sulphuric acid, proves to be 2-*quinolyl*-2-*isoquinolyl ketone*, $C_9NH_6 \cdot CO \cdot C_9NH_6$. It yields *iso*quinoline and quinaldic acid by heating with concentrated potassium hydroxide. It forms a *methiodide*, $C_{20}H_{15}ON_2I$, decomp. about 120°, and an *ethiodide*, decomp. about 160°. By treatment with aqueous silver sulphate, the methiodide yields a solution of the methosulphate, which is treated

with sodium hydroxide and potassium ferricyanide, whereby quinaldic acid and N-methyl-*iso*quinolone are produced. By reduction with alcoholic ammonium sulphide at 200°, *iso*quinoline red yields benzyl mercaptan and a *substance*, m. p. 231°, golden-yellow leaflets.
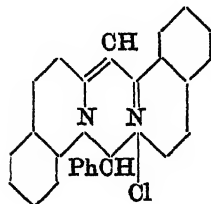
The preceding statements, together with the fact that the quinaldine cannot be replaced by lepidine or any other methylated quinoline in the preparation of *iso*quinoline red, lead to the annexed formula for this substance.

<div style="text-align:right">C. S.</div>

Octachloroindigotin and Some Derivatives of Tetrachloro-anthranilic and Tetrachlorophthalic Acids. WILLIAM R. ORN-DORFF and E. H. NICHOLS (*Amer. Chem. J.*, 1912, **48**, 473—500).—By the action of dimethylaniline on the product of the diazotisation of tetrachloroanthranilic acid (Villiger and Blangey, A., 1909, i, 922), *dimethylaminobenzeneazotetrachlorobenzene-o-carboxylic acid*,

$$NMe_2 \cdot C_6H_4 \cdot N:N \cdot C_6Cl_4 \cdot CO_2H,$$
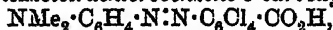
is obtained as a brilliant red substance. The *acetyl* derivative of 5:6:7:8-tetrachloro-3:4-dihydro-2:4-benzoxaz-1-one (Villiger and Blangey, *loc. cit.*), m. p. 166·5° (corr.), crystallises in colourless, rectangular plates. When tetrachlorophenylglycine-o-carboxylic acid (A., 1910, i, 382) is boiled with acetic anhydride, *tetrachloroacetyl-indoxylic acid*, $C_6Cl_4 \begin{smallmatrix} NAc \\ C(OH) \end{smallmatrix} C \cdot CO_2H$, m. p. 225° (corr.), is produced as a pale yellowish-green, crystalline powder; its *silver* salt forms light greyish-green needles containing $1H_2O$. If fused sodium acetate is used with the acetic anhydride, the reaction proceeds further, and mono- and di-acetyl derivatives of tetrachloroindoxyl are produced; the *acetyl* derivative, $C_6Cl_4 \begin{smallmatrix} NAc \\ C(OH) \end{smallmatrix} CH$, m. p. 195° (uncorr.), crystallises in white, slender, microscopic prisms; the *diacetyl* derivative, $C_6Cl_4 \begin{smallmatrix} NAc \\ C(OAc) \end{smallmatrix} CH$, m. p. 167° (uncorr.), forms very pale blue, rectangular prisms. On heating a solution of tetrachloroacetylindoxylic

<div style="text-align:right">h 2</div>

acid in aqueous ammonia, *octachloroindigotin*,

$$C_6Cl_4 \underset{CO}{\overset{NH}{<}} > C:C \underset{NH}{\overset{CO}{<}} > C_6Cl_4,$$
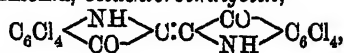
is produced as a purple, amorphous precipitate, which, when heated in a current of air at 360°, sublimes in small, rhombic plates.

Villiger's statement (A., 1909, i, 931) that dichlorophthalylhydroxyl-amine is converted into dichloroanthranilic acids by heating it with sodium carbonate solution, suggested that tetrachloroanthranilic acid might be similarly obtainable from the corresponding tetrachloro-phthalylhydroxylamine (tetrachlorophthaloxime), and the following experiments were, therefore, carried out. When tetrachlorophthalic anhydride is heated with a solution of hydroxylamine in methyl alcoho *tetrachlorophthaloxime hydroxide methyl ether,*

$$CO \underset{C_6Cl_4}{\overset{O}{<}} > C(OH) \cdot NH \cdot OMe,$$
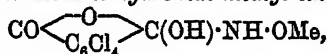
m. p. 2'6—247° (corr., decomp.), is produced. If the tetrachlorophthalic ar¹...de is heated with an aqueous solution of hydroxylamine, *tetrachlorophthaloxime hydroxide,* $CO \underset{C_6Cl_4}{\overset{O}{<}} > C(OH) \cdot NH \cdot OH$, m. p. 254° (corr.), is obtained, which crystallises in nearly white prisms. When this substance is heated at 50° or left in a vacuum desiccator with phosphoric oxide, it loses water and becomes converted into *tetra-chlorophthaloxime,* $C_6Cl_4 \underset{C(:NOH)}{\overset{CO}{<}} > O$, which forms lemon-yellow prisms; the *sodium* salt is described; the *acetyl* derivative, m. p. 176° (corr.), crystallises in white needles.   E. G.

[**Preparation of Halogenated Derivatives of Indigoid Com-pounds.**] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 252387).—The bisulphite compounds of indigoid derivatives are readily halogenated, yielding *compounds* with a high halogen content. The bromination of the bisulphite compounds obtained from isatin chloride and carbazole, and of that from indoxyl-red,

$$C_6H_4 \underset{CO-}{\overset{NH}{<}} > C:C \underset{C_6H_4}{\overset{-CH}{<}} > N,$$
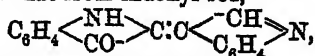
is described, and other compounds which can be similarly treated are mentioned.   F. M. G. M.

Preparation of Condensation Products from Indigotin, its Homologues or Halogen-substitution Products. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 250744).—When indigotin, its homologues, or halogen-substitution products are heated at 150—200° in the presence of zinc chloride with benzoic anhydride (or substituted benzoic anhydrides), condensation products are formed which find employment in the preparation of dyes.

Indigotin (10 parts), zinc chloride (10 parts), and benzoic anhydride (40 parts) at 150—160° yield a yellow, crystalline *compound*, m. p. 357°.

The following analogous *compounds* are also described: from di-bromoindigotin with benzoic anhydride, yellow crystals, m. p. 340° (about) from indigotin with *p*-toluic anhydride, pale yellow crystals,

m. p. 330°; from the same with dibromoindigotin, m. p. above 330°: from indigotin with p-methoxybenzoic anhydride, yellow crystals, m. p. 320°; and from indigotin with o-chlorobenzoic anhydride, m. p. above 340°. These compounds dissolve in concentrated sulphuric acid with red colorations, but are insoluble in alkaline hyposulphite; they can be prepared in the presence of an indifferent solvent or by the fusion of the constituents. F. M. G. M.

Buchner's Pyrazolinecarboxylic Acids. CARL BÜLOW (*Ber.*, 1912, **45**, 3349—3355).—A reply to Darapsky's criticism (A., 1912, i, 391) of the author's view that the additive products of ethyl diazoacetate with olefinic esters are really open-chain compounds (A., 1912, i, 134, 316). D. F. T.

Condensation Product of Formaldehyde, Ammonia, and Antipyrine. CARL MANNICH and W. KRÖSCHE (*Arch. Pharm.*, 1912, 250, 647—667).—Antipyrine condenses with formaldehyde and ammonia, or with the hexamethylenetetramine formed from these two substances, to give triantipyryltrimethyleneamine,

$$N(CH_2 \cdot O \cdot C_{11}H_{11}N_2)_3,$$
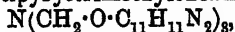
in the formation of which antipyrine is believed to react in the enolic form represented by the formula $NPh\begin{smallmatrix}C(OH)\colon C\\ | \quad | \\ NMe{-}CMe\end{smallmatrix}$. A similar condensation occurs with antipyrine derivatives so long as these are not substituted in position 4.

Triantipyryltrimethyleneamine hydrochloride, $C_{36}H_{40}O_3N_7Cl,6H_2O$, m. p. 178°, or 206° (dry), formed when the condensation is effected by hydrochloric acid, is crystalline. The free base, m. p. 259—260°, crystallises anhydrous from methyl alcohol. When boiled with hydrochloric acid, it yields formaldehyde, ammonia, and methylenebisantipyrine, which yields a trihydrated dihydrochloride (Schuftan, A., 1895, i, 482), and a *monohydrochloride*, $CH_2(C_{11}H_{11}ON)_2,HCl,3H_2O$, m. p. 94—95°, which on drying at atmospheric temperature over sulphuric acid becomes *anhydrous*, then melts at 100—110°, and on solution in acetone deposits some *anhydrous dihydrochloride*, m. p. 200—220°, leaving some free base in solution.

On treatment with sodium hydrogen sulphite and sulphurous acid, triantipyryltrimethyleneamine yields antipyrine, which appears to be formed direct from the parent substance, since sulphurous acid has no action on methylenebisantipyrine.

Tritolypyryltrimethyleneamine, $C_{39}H_{45}O_3N_7,7H_2O$, m. p. 214—215° (dry), formed by condensing hexamethylenetetramine with tolypyrine (p-tolyl-2 : 3-dimethyl-5-pyrazolone), crystallises from a mixture of methyl alcohol and water; the *hydrochloride*, $C_{39}H_{40}O_3N_7Cl,6H_2O$, m. p. 100—105°, or 191° (dry), forms short, stout needles. Sulphurous acid in presence of sodium hydrogen sulphite hydrolyses it to tolypyrine, whilst hydrochloric acid converts it into ammonia, formaldehyde, and *methylenebistolypyrine*, m. p. 183—186°, or 190° (dry), which crystallises from 80% alcohol in slender needles, and can be prepared by condensing tolypyrine with formaldehyde.

Trihomoantipyryltrimethyleneamine, m. p. 280°, similarly obtained, crystallises from boiling methyl alcohol ; the *hydrochloride,* m. p. 202°, crystallises from acetone. *Methylenebishomoantipyrine* crystallises from ethyl acetate in tablets with $1H_2O$, m. p. 120—130°, and after drying over sulphuric acid melts at 105—106°. The *dihydrochloride,*

$$C_{25}H_{30}O_2N_4Cl_2,3H_2O,$$
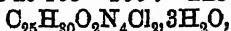
separates from 10% hydrochloric acid in stout crystals, m. p. 200—210°.

T. A. H.

Substituted α-Hydroxy- and α-Methyl-benziminazoles. OTTO KYM and L. RATNER *(Ber.,* 1912, **45,** 3238—3255. Compare A., 1904, i, 453 ; 1911, i, 1044).—*p*-Nitro-*o*-phenylenediamine reacts readily with carbamide, forming 5-nitro-2-hydroxybenziminazole,

$$NO_2 \cdot C_6H_3 {\overset{NH}{\underset{N}{\big<}}} C \cdot OH$$
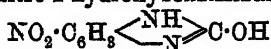
(compare Hager, A., 1885, 149). This reacts with phosphoryl chloride forming 2-chlorobenziminazole, from which the 2-hydroxy-compound is regenerated on boiling with concentrated hydrochloric acid. Ammonia or aniline converts it into corresponding 2-amino- or 2-anilino-derivatives. The property of the azo-dyes of all phenylated benziminazoles to dye cotton persists, although to a less degree, in the 2-hydroxy-compounds.

Both 2-hydroxyl- and 2-methyl-benziminazoles can be nitrated without difficulty, forming dinitro-derivatives. It was found impossible to open the iminazole ring in these by Bamberger's method—by means of benzoyl chloride and sodium hydroxide.

Dinitro-2-hydroxybenziminazole when heated with aniline yields nitro-2-hydroxyanilinobenziminazole,

$$NHPh \cdot C_6H_2(NO_2) {\overset{NH}{\underset{N}{\big<}}} C \cdot OH,$$
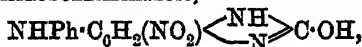
a red, crystalline compound, whereas the mononitro-2-hydroxybenziminazole does not react with aniline. This behaviour indicates that the second nitro-group has entered in the ortho-position to the first.

On reduction of the dinitro-compounds the diamino-compounds obtained behave as *o*-diamines, forming azimino-derivatives with nitrous acid and the corresponding dianhydro-derivatives when boiled with acetic acid. 2 : 7-Dimethylbenzdi-iminazole,

$$CMe {\overset{NH}{\underset{N}{\big>}}} C_6H_2 {\overset{NH}{\underset{N}{\big<}}} CMe,$$
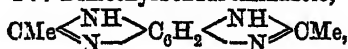
is shown to be identical with Nietzki's (A., 1887, 476, 477) diethenyl base obtained by nitration and reduction of diacetyl-*m*-phenylenediamine.

When 5 : 6-diamino-2-methylbenziminazole is fused with carbamide the dihydro-derivative already mentioned, 7-hydroxy-2-methylbenzdi-iminazole, $CMe {\overset{NH}{\underset{N}{\big>}}} C_6H_2 {\overset{NH}{\underset{N}{\big<}}} C \cdot OH$, is formed. These changes confirm the structure of dinitro-2-hydroxybenziminazole as

$$\overset{NO_2}{\underset{NO_2}{}} {\Large\bigcirc} {\overset{-NH}{\underset{-NH}{\big>}}} C \cdot OH.$$
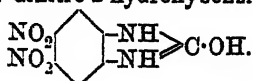
5-Nitro-2-hydroxybenziminazole crystallises in yellowish-white needles,

m. p. 308°; it is strongly acid, dissolving in alkali hydroxide with an intense orange-yellow coloration. It further has weak basic properties.

5 : 6-*Dinitro-2-hydroxybenziminazole* separates in centimetre-long, lustrous needles, m. p. above 300°; the solution in cold dilute alkali hydroxide is intense red, and it forms a deep red, crystalline sodium salt.

5 : 6-*Dinitro-2-methylbenziminazole* forms yellowish-white needles, m. p. 223°.

Nitro-2-hydroxyanilinobenziminazole crystallises in red platelets, m. p. 298°.

Nitroamino-2-hydroxybenziminazole, prepared by heating the dinitro-compound with ammonia at 180—210°, forms bright red, lustrous crystals, m. p. above 300°; it is soluble in concentrated hydrochloric acid, and also dissolves in dilute sodium hydroxide or ammonia with a deep red coloration.

5 : 6-*Diamino-2-hydroxybenziminazole* readily oxidises as free base ; the *hydrochloride* forms a brown, microcrystalline powder ; the *diacetyl* derivative crystallises in lustrous, silky needles, m. p. 293—294° ;

2-*hydroxybenzdi-iminazole*, $N<^{NH}_{N}>C_6H_2<^{NH}_{N}>C\cdot OH$, crystallises in yellow platelets, m. p. above 300°.

5 : 6-*Diamino-2-methylbenziminazole* crystallises in pale brown needles, m. p. above 300°; the *diacetyl* derivative separates in slightly pink-coloured, glistening needles, also m. p. above 300°. 2-*Methylbenzdi-iminazole* forms reddish-brown, stunted needles, m. p. above 300°.

2 : 7-*Dimethylbenzdi-iminazole* is obtained in lustrous, yellowish-white needles, m. p. outside the thermometer range.

7-*Hydroxy-2-methylbenzdi-iminazole* also forms lustrous, yellowish-white platelets, m. p. above 300°.

2-*Chloro-5-nitrobenziminazole* is a yellow, crystalline powder, m. p. 222—223°.

5-*Nitro-2-anilinobenziminazole* yields tiny, brown crystals, m. p. 278°.

5-*Nitro-2-aminobenziminazole* crystallises in a bulky mass of slender, yellow needles, m. p. 189—190°; the *acetyl* derivative is colourless.

E. F. A.

Constitution of Compounds from o-Diamines and α-Hydroxy-acids. Acetylation of Benziminazoles. AUGUSTIN BISTRZYCKI and GEORG PRZEWORSKI (*Ber.*, 1912, **45**, 3483—3495).—The product obtained by the interaction of 3 : 4-tolylenediamine and lactic acid is regarded as a tetrahydroquinoxaline by Georgescu, and as a benzimin-azole by Hinsberg. The authors now show that the latter view is correct and that the reaction is a general one ; thus o-phenylenediamine and mandelic acid (1¼ mol.) at 130—135° yield 2-α-hydroxybenzyl-benziminazole ; o-phenylenediamine and lactic acid (3 mols.) at 105—110° yield 2-α-hydroxyethylbenziminazole ; 3 : 4-tolylenediamine and mandelic acid (1¼ mol.) at 130—135° yield 2-α-hydroxybenzyl-5-methylbenziminazole, and 3 : 4-tolylenediamine and lactic acid yield 5-methyl-2-α-hydroxyethylbenziminazole. These substances are identical with Georgescu's so-called tetrahydroquinoxalones.

o-Phenylenediamine and glycollic acid at 120° yield 2-*hydroxymethyl-*

benziminazole, $C_6H_4<^{NH}_{N}>C\cdot CH_2\cdot OH$, m. p. 171—172°, colourless plates, which forms an *acetyl* derivative, m. p. 99—101°, by boiling with acetic anhydride and sodium acetate, and is oxidised by hot dilute alkaline potassium permanganate to *benziminazole-2-carboxylic acid*,

$$C_8H_6O_2N_2, 2H_2O,$$

decomp. 169°, long prisms (*barium* salt, $C_{16}H_{10}O_4N_4Ba$), from which benziminazole is obtained by heating at 169°. The authors find that benziminazoles are readily acetylated by heating with acetic anhydride; thus benziminazole or benziminazole-2-carboxylic acid yields 1-*acetylbenziminazole*. m. p. 113—114°, long, prismatic needles, and 2-methylbenziminazole yields 1-*acetyl-2-methylbenziminazole*, m. p. 85—86°, colourless, microscopic needles or prisms.

3 : 4-Tolylenediamine and glycollic acid yield 5-*methyl-2-hydroxymethylbenziminazole*, m. p. 203°, plates or needles (*acetyl* derivative, m. p. 129—132°), from which Hinsberg's 5-methylbenziminazole-2-carboxylic acid, m. p. 156° (decomp.), is obtained by oxidation.

By oxidation with chromic and acetic acids, 2-α-hydroxybenzylbenziminazole yields 2-*benzoylbenziminazole*, $C_6H_4<^{NH}_{N}>C\cdot COPh$, m. p. 209—210° (decomp.), microscopic needles (*phenylhydrazone*, m. p. 185—186°, yellow plates; *phenylmethylhydrazone*, m. p. 225°, yellow prisms), and 2-α-hydroxybenzyl-5-methylbenziminazole yields 2-*benzoyl-5-methylbenziminazole*, m. p. 140—141°, felted needles.

Equal molecular quantities of *o*-phenylenediamine and benzilic acid at 150—160°, or *o*-phenylenediamine (1·5 mol.) and chlorodiphenylacetic acid under the same conditions, yield a *substance*, $C_{20}H_{16}ON_2$, m. p. 221—223°, microscopic plates, which is probably 2-*hydroxydiphenylmethylbenziminazole*, $C_6H_4<^{NH}_{N}>C\cdot CPh_2\cdot OH$. The 5-methyl *homologue*, m. p. about 255°, is obtained from 3 : 4-tolylenediamine and chlorodiphenylacetic acid, whilst diphenylacetic acid and *o*-phenylenediamine yield 2-*benzhydrylbenziminazole*, $C_6H_4<^{NH}_{N}>C\cdot CHPh_2$, m. p. 218—220°, colourless, prismatic needles.   C. S.

The Constitution of Acetyl-β-anthraquinonylmethylpyrazolone. RICHARD MÖHLAU (*Ber.*, 1912, **45**, 3596).—The pyrazolone described recently (Möhlau, A., 1912, i, 704) is 4-acetyl-1-β-anthraquinonyl-3-methylpyrazolone.   D. F. T.

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. ALFRED SCHAARSCHMIDT (D.R.-P. 251480). —When *o*-diaminoanthraquinones are condensed with benzanthrone or anthraquinone, ω-di- or ·ω-tri-halogenmethyl derivatives, aldehydes, carboxylic acids, or their chlorides, they furnish iminazole condensation derivatives.

Compounds from the condensation of 1 : 2-diaminoanthraquinone with anthraquinone-2-carboxylic acid and with *benzanthronecarboxylic acid* (a yellow powder obtained from *p*-tolyl-*o*-benzoic acid, glycerol, and sulphuric acid), and from 2 : 3-diaminoanthraquinone with ω-dichloro-β-methylanthraquinone are described.   F. M. G. M.

Preparation of Anthraquinone Derivatives containing Nitrogen. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252529).—The action of aldehydes on aryl-*o*-aminoanthraquinones has previously been described (A., 1907, i, 1085) ; when these are replaced by ketones the following action occurs :

$$A{<}^{\text{NHPh}}_{\text{NH}_2} + R{\cdot}CO{\cdot}R' = A{<}^{\text{NH}-}_{\text{N}-} \bigcirc + H_2O,$$
$$R{\cdot}CHR'$$
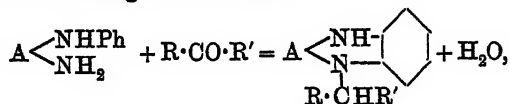
where A = anthraquinone, and R' and R aryl or alkyl.

3-Bromo-2-amino-1-*p*-toluidinoanthraquinone (10 parts) when boiled with acetone (10 parts), zinc chloride (5 parts), and acetic acid (100 parts) yields a *compound*, bluish-red needles with metallic lustre ; whilst *compounds* from the same base with acetophenone, and with isatin (blue needles), and from 3 : 7-dibromo-2 : 6-diamino-1 : 5-dianilinoanthraquinone with acetone are described in the original. These compounds all furnish soluble *sulphonic acids*, which dye wool in blue shades. F. M. G. M.

[**Preparation of Anthracene Derivatives.**] FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 251021).—When the dyes obtained from di- and tri-anthrimides by the action of aluminium chloride are treated (in a paste) with sodium hypochlorite at 80° new compounds are formed.

$$C_6H_4{<}^{\text{CO}-}_{\text{CO}-} \bigcirc {-}N{\cdot}C_{14}H_7O_2$$
$$C_{14}H_7O_2{\cdot}N{-} \bigcirc {<}^{\text{CO}}_{\text{CO}}{>}C_6H_4$$
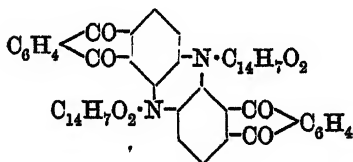
Dianthraquinonylindanthren, $C_{56}H_{26}O_8N_2$ (annexed formula), orange-yellow needles, which decomposes at high temperatures with partial sublimation, is thus obtained from the product furnished by *aa*-dianthrimide ; whilst the dye from 1 : 5-di-*a* : *a*-anthriminoanthraquinone and aluminium chloride yields under similar conditions a *compound* consisting of a reddish-brown powder. F. M. G. M.

Indamines. FRITZ ULLMANN and JOHANN GNAEDINGER (*Ber.*, 1912, **45**, 3437—3446).—Indamines are readily obtained by passing air through a cold dilute aqueous solution of equal molecular quantities of a meta-diamine and *p*-aminophenol hydrochloride after the addition of dilute sodium hydroxide (2 mols.) ; thus *m*-tolylenediamine and *p*-aminophenol yield 2-*amino-4'-hydroxy-5-methylindamine,*

$$NH{:}C_6H_2Me(NH_2){:}N{\cdot}C_6H_4{\cdot}OH,$$
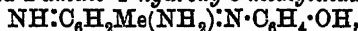
decomp. about 165°, green metallic needles containing $3H_2O$. It is readily soluble in aqueous sodium hydroxide, and by reduction with alkaline sodium hyposulphite yields 2 : 4-*diamino-4'-hydroxy-5-methyldiphenylamine,* $C_6H_3Me(NH_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}OH$, m. p. 215°, colourless crystals (*sulphate,* $C_{18}H_{15}ON_3,H_2SO_4$, m. p. 202°). By the prolonged passing of air through its suspension in hot water, the indamine is converted into the *phenazine,* $NH_2{\cdot}C_6H_2Me{<}^{\text{N}}_{\text{N}}{>}C_6H_3{\cdot}OH$, m. p.

above 360°, red needles with green reflex (*hydrochloride*, m. p. above 360°, red needles with green reflex; *diacetyl* derivative, m. p. 291°, darkening at 282°, yellow crystals).

m-Phenylenediamine and *p*-aminophenol yield Nietzki's so-called aminoindophenol, which, however, on account of its solubility in sodium hydroxide, is more suitably regarded as the hydroxyindamine, $NH:C_6H_3(NH_2):N\cdot C_6H_4\cdot OH$. The phenazine obtained by its further oxidation has m. p. above 360°, not 268° as given by Nietzki; also the diacetyl derivative has m. p. 275°, not 258°.

3'-Chloro-2-amino-4'-hydroxy-5-methylindamine,
$$NH:C_6H_2Me(NH_2):N\cdot C_6H_3Cl\cdot OH,$$
m. p. 185°, metallic violet needles containing H_2O, obtained from *m*-tolylenediamine and 2-chloro-*p*-aminophenol, yields *3'-chloro-2 : 4-diamino-4'-hydroxy-5-methyldiphenylamine*, m. p. 212°, colourless needles, by reduction, and the *phenazine*, $C_{13}H_{10}ON_3Cl$, m. p. above 360° (*diacetyl* derivative, m. p. 274°), by oxidation.

6-Chloro-*m*-phenylenediamine and *p*-aminophenol yield the *indamine*, $NH:C_6H_2Cl(NH_2):N\cdot C_6H_4\cdot OH$, decomp. 108°, metallic violet crystals containing H_2O (the corresponding *phenazine* and its *diacetyl* derivative have m. p. above 360° and 307° respectively), whilst 6-chloro-*m*-phenylenediamine and 2-chloro-*p*-aminophenol yield the *indamine*,
$$NH:C_6H_2Cl(NH_2):N\cdot C_6H_3Cl\cdot OH,$$
decomp. 128°, metallic violet needles containing H_2O.

By a similar process of oxidation, α-naphthol and *p*-aminophenol yield the *dihydroxyindonaphthol*, $OH\cdot C_6H_4\cdot N:C\underset{:CH:C(OH)}{\overset{C_6H_4}{<}}>CO$, m. p. 298°, glistening, green leaflets changing to a red powder at 120°. This substance, the constitution of which is proved by its formation from potassium β-naphthaquinone-4-sulphonate and *p*-aminophenol hydrochloride in cold aqueous solution, condenses with *o* phenylenediamine in alcoholic solution to form the *hydroxyanilinonaphthazine*,
$$OH\cdot C_6H_4\cdot NH\cdot C_{10}H_5\underset{N}{\overset{N}{<}}>C_6H_4,$$
m. p. 291°, orange crystals.   C. S.
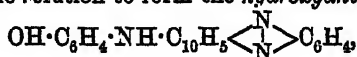
Synthesis of 1 : 3 : 7-Naphtha*iso*triazines : Derivatives of a New Heterocyclic System. MARSTON T. BOGERT and HARRY LINN FISHER (*J. Amer. Chem. Soc.*, 1912, **34**, 1576—1580).—In another paper (this vol., i, 98) the authors have described 5-aminoquinoline-6-carboxylic acid, its acetyl derivative, and the lactam of the latter. From these substances, compounds have been prepared containing the new nucleus (annexed formula), which is designated the 1 : 3 : 7-naphtha*iso*triazine nucleus.

2 : 3-*Dihydro*-1 : 3 : 7-*naphthaisotriazine*-4-*one* (4-*hydroxy*-1 : 3 : 7-*naphthaisotriazine*),
$$\underset{-NH\cdot CO}{\overset{CH=N}{>}}C_9NH_5 \rightleftharpoons \underset{N:C(OH)}{\overset{CH=N}{>}}C_9NH_5,$$
m. p. 298·7° (corr.), obtained in 10% yield by heating 5-aminoquinoline-6-carboxylic acid with excess of formamide at 140° in
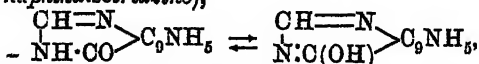
a sealed tube, crystallises in lustrous, pink prisms. The *2-methyl* derivative, m. p. above 300° (decomp.), prepared by boiling the lactam of 5-acetylaminoquinoline-6-carboxylic acid with solution of ammonia, forms slender, yellow needles, and, when heated with benzaldehyde and a few drops of acetic anhydride, yields the *2-styryl* derivative, $CHPh:CH \cdot C_{11}H_6ON_3$, m. p. above 300° (decomp.), as a yellow, crystalline powder. The 2 : 3-*dimethyl* derivative,

$$\begin{matrix} CMe = N \\ NMe \cdot CO \end{matrix} > C_9NH_5,$$
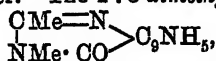
m. p. 178° (uncorr.), prepared by the action of methylamine on the lactam, crystallises in long, yellow needles. The *2-methyl-3-ethyl*, *2-methyl-3-n-propyl*, *3-phenyl-2-methyl*, and *3-p-anisyl-2-methyl* derivatives have m. p. 152·5° (uncorr.), 121—122° (uncorr.), 263—263·5° (corr.), and 246·9—247·9° (corr.) respectively. The *3-amino-2-methyl* derivative, m. p. 256·7° (corr.), obtained by the action of hydrazine on the lactam, is colourless; the *3-acetylamino-2-methyl* derivative has m. p. 268·5—269·5° (corr.), and the *3-benzylideneamino-2-methyl* derivative, m. p. 222·6° (corr.). The *3-anilino-2-methyl* derivative, $\begin{matrix} CMe = N \\ N(NHPh) \cdot CO \end{matrix} > C_9NH_5$, m. p. 249·5—250·5° (corr.), crystallises in pale brown needles.

1 : 2 : 3 : 4-*Tetrahydro*-1 : 3 : 7-*naphthaisotriazine*-2 : 4 -*dione*   (2 : 4-*dihydroxy*-1 : 3 : 7-*naphthaisotriazine*),

$$\begin{matrix} CO \cdot NH \\ NH \cdot CO \end{matrix} > C_9NH_5 \rightleftharpoons \begin{matrix} C(OH):N \\ N:C(OH) \end{matrix} > C_9NH_5,$$
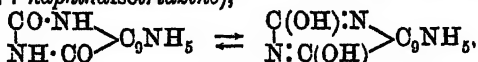
m. p. above 300°, is obtained as a yellow or brown powder by fusing a mixture of 5-aminoquinoline-6-carboxylic acid and carbamide.

E. G.

[**Preparation of Anthracene Derivatives.**] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 253088).—It is found that the previously described ψ-azimino-compounds (A., 1912, i, 1035) obtained by oxidising the azo-compound formed by coupling 2-aminoanthracene with diazotised 2-aminoanthraquinone can be nitrated, and the so-obtained *nitro-* or *dinitro-*compounds reduced with sodium sulphide or alkaline sodium hyposulphite to the corresponding *amino-* or *diamino-*compounds. The nitrated products are greenish-yellow, and the amino-derivatives, brownish-black, powders.

F. M. G. M.

Methyliminothiotriazine. ADRIANO OSTROGOVICH (*Chem. Zentr.*, 1912, ii, 607 ; from *Bull. Soc. Şti. Bucureşti*, 1912, 21, 27—31).—The 2-imino-6-thiol-4-methyl-1 : 3 : 5-triazine, already described (A., 1912, i, 320), on oxidation with nitric acid (D 1·4) yields cyanuric acid, and with alkaline permanganate gives iminoketomethyltriazine (A., 1904, i, 832), the picrate of which melts at 221—221·5°, not 121—121·5° as stated previously. Iminothiolmethyltriazine does not give up its sulphur to mercuric oxide, but yields a stable mercury salt when mercuric chloride is added to its solutions in aqueous sodium hydroxide.

T. A. H.

Quadriurates. WILLEM E. RINGER and J. I. J. M. SCHMUTZER (*Zeitsch. physiol. Chem.*, 1912, 82, 209—220. Compare Kohler, A., 1911, i, 243, 690).—The hypothesis that the so-called quadriurates are mixed crystals has been tested experimentally, a series of quadriurates of varying composition having been examined chemically and crystallographically. This hypothesis is satisfactory when it is assumed that the urates represent solid solutions of uric acid in ordinary mono-metal urates, which are formed at high temperatures, but are unstable at lower temperatures, and tend to part with the excess of uric acid.

E. F. A.

Preparation of Aminobenzoylamino-compounds FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252376) —When sodium diaminobenzoyldiaminostilbenedisulphonate is fused during half an hour with *p*-nitrobenzoyl chloride and the *di*-p-*nitrobenzoyl* derivative subsequently reduced with iron and acetic acid, it furnishes the compound, $C_2H_2[C_6H_8(SO_3Na)\cdot NH\cdot CO\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot NH_2]_2$.

Other analogous compounds with valuable tinctorial properties can be obtained in the benzidine, tolidine, or dianisidine series.

F. M. G. M.

Separation of Proteoses by Ultra-filtration. EDGARD ZUNZ (*Bull. Acad. roy. Belg.*, 1912, 656—674. Compare A., 1911, i, 1050). —The composition of the filtrate obtained from identical solutions of Witte's peptone, submitted under the same conditions to Bechhold's method of ultra-filtration, varies appreciably from filter to filter, although the latter are made as alike as possible. Further, the filtrate varies during the course of the same experiment, at one time the ultra-filter allowing certain proteoses to pass and at another time retaining a portion of them. The four groups of proteoses established by Pick cannot be satisfactorily separated by successively employing ultra-filters with smaller and smaller pores. The ultra-filtration causes a dissociation of each of these groups of proteoses into several fractions. In these groups the proteoses, the aliphatic amino-nitrogen of which can be detected by van Slyke's method, pass completely through an ultra-filter made by means of a 6% collodion solution.   W. G.

Changes in the Physical Conditions of Colloids. XIV. The Hydration of Various Protein Compounds, with Special Reference to the Action of Caffeine. WOLFGANG PAULI and OSKAR FALEK (*Biochem. Zeitsch.*, 1912, 47, 270—299).—The general theory of Pauli's as to the high degree of hydration of the protein ion is confirmed by a series of measurements of the changes of viscosity of well dialysed gelatin solutions on addition of acids and alkalis, in both of which cases well-marked maxima are observed. According to the theory, salts combine with the protein, and when these are present, the number of free proteins ions is diminished. The addition of salts diminishes the viscosity, and this effect was quantitatively measured in the case of several salts.

Caffeine has, however, a peculiar action on the ox- and horse-serum proteins, in that it increases the viscosity of the acid-protein mixtures

(and according to Pauli the state of hydration in solution). This effect has been measured in a large number of cases. The magnitude of the effect is also influenced by the nature of the acid employed. A similar effect was produced by theophylline, but not by diethylglycin-amine caffeine or caffeine ethylenediamine, both of which produce a depression of viscosity. Caffeine does not effect the hydration of gelatin or fibrin, as it does not cause these substances to take up more water. The reason of the peculiar action of caffeine on certain proteins may be due to formation of complex double compounds. It does not appear to be due to direct salt formation, as determined by the effect of addition of caffeine to protein solutions on the electro-lytic conductivities, the osmotic pressures, or the hydrogen-ion concen-trations as measured by the electrometric method. S. B. S.

The Oxidation Relations of Certain Heavy Metals in Com-bination with Protein, and Some Physico-chemical Properties of the Same. II. CARLO CERVELLO and CORRADO VARVARO (*Arch. expt. Path. Pharm.*, 1912, 70, 369—374).—The coagulation rate of zinc albuminate and mercury albuminate is greater than that of the simple protein, but less than that of the albuminates of manganese and copper. Iron albuminate is not altered by boiling. Complete coagulation with precipitation of denaturated protein is only obtained with zinc albuminate. In weakly acid or neutral solutions, the other metallic albuminates give only a cloudy fluid on heating : this is most marked with mercury, and least with manganese albuminate. In reference to their oxidative powers, as measured by the effect on indigotin and similar substances, the albuminates of iron and copper are most energetic ; those of mercury, zinc, and manganese follow in the order named. The albuminates therefore behave like simple metallic salts. W. D. H.

The Kyrine Fraction obtained on Partial Hydrolysis of Proteins. I. PHŒBUS A. LEVENE and F. J. BIRCHARD (*J. Biol. Chem.*, 1912, 13, 277—289).—Siegfried's hypothesis regarding kyrine is that it is a fragment of the protein molecule which resembles natural protamines. The kyrine fraction obtained in the present research by Siegfried's method of partial hydrolysis of gelatin yielded on hydrolysis arginine, lysine, glutamic acid, glycine, and proline in peptide linking. Probably two peptides were present, one con-taining lysine and three monoamino-acids, and the other, arginine and one monoamino-acid. Further investigations are being prosecuted. W. D. H.

The Isoelectric Point of Casein. LEONOR MICHAELIS and H. PECHSTEIN (*Biochem. Zeitsch.*, 1912, 47, 260—268).—The isoelectric point was determined by ascertaining the optimal mixture for precipi-tation of sodium acetate and acetic acid solutions, and also by the method of electrocataphoresis. In the former case the salt concen-trations in the various series of experiments were kept constant, and in the latter case, the salt content was kept very low. By these methods the isoelectric point was found to be $2·5 \times 10^{-5}$ and $2·4 \times 10^{-5}$.

respectively. In the presence of salts a certain asymmetry of behaviour was observed, in that after twenty-four hours excess of acid above the isoelectric point allowed greater precipitation than deficit of acid.

S. B. S.

Blood Pigment. LÉON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1912, 82, 413—414. Compare Grabowski and Marchlewski, A., 1912, i, 1015).—The conclusion that hæmopyrrole whether derived from blood pigment or chlorophyll contains 3-methyl-4-ethylpyrrole is confirmed by Piloty and Stock (A., 1912, i, 923), who obtain the same substance from hæmin. The synthesis of chlorophyll in plants begins probably with that of 3-methyl-4-ethylpyrrole.   E. F. A.

Nomenclature of Derivatives of the Blood Pigment. KARL BURKER (*Zeitsch. physiol. Chem.*, 1912, 82, 346).—Instead of Abderhalden's (A., 1912, i, 521) nomenclature of hæmatin for hæmochromogen and oxyhæmatin for hæmatin, it is suggested to use the terms reduced hæmatin and oxyhæmatin.   E. F. A.

Methylation of Hæmin. IV. WILLIAM KUSTER (*Zeitsch physiol Chem.*, 1912, 82, 113—159).—In the preparation of hæmin by Mörner's method using methyl alcohol, a crude product is obtained in satisfactory amount containing very little protein, which usually consists mostly of methylhæmin mixed with a little dimethylhæmin. There is evidence that there are two methylhæmins, one or the other being formed from ox-blood according to the conditions. One isomeride is insoluble in 5% sodium carbonate; the other is soluble in sodium carbonate, and also in 0·7% potassium carbonate. The dissolved dye contains chlorine.

The first isomeride loses chlorine without dissolving, and forms a methylhæmatin; a similar compound is formed by the action of methyl-alcoholic sodium hydroxide.

The dehydrochloride products prepared from the methylhæmins are of different composition, the one being normal, the other having taken up a molecule of water.

Methylhæmatin and hæmatin when dissolved in methyl alcohol containing sulphuric acid and the boiling solution precipitated by hydrochloric acid yield dimethylated products which do not contain the calculated proportion of chlorine for hæmin derivatives and are soluble in acidified methyl alcohol. Dehydrochloromethylhæmin under similar treatment does not show a complete addition of hydrogen chloride.

Dehydrochlorohæmin is converted into dimethylhæmin. Dimethylhæmin forms a dimethylated dehydrochloro-product.

Methylhæmin is hydrolysed by more than three molecules of 1% sodium hydroxide in the cold; dimethylhæmin requires warming to effect hydrolysis. Dimethylhæmin is readily converted into dimethylhæmatin by the action of methyl alcoholic sodium hydroxide.

E. F. A.

Preparation of Hæmatoporphyrin from Carbon Monoxide Blood. VINZENZ ARNOLD (*Zeitsch. physiol. Chem.*, 1912, 82, 273—275). —Pure hæmatoporphyrin, particularly suited for spectroscopic work and free from brown-coloured impurities, is obtained by completely replacing the oxygen in blood by carbon monoxide before acting on it with sulphuric acid.   E. F. A.

Formation of Porphyrin. HANS FISCHER and FRIEDRICH MEYER-BETZ (*Zeitsch. physiol. Chem.*, 1912, 82, 96—108).—The exact conditions for the preparation of mesoporphyrin are described. On oxidation with lead peroxide in acid solution, methylethylmaleinimide,

$$NH\!\!<\!\!{}^{CO \cdot CEt}_{CO \cdot CMe},$$
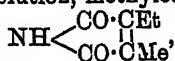
and hæmatic acid, $NH\!\!<\!\!{}^{CO \cdot CMe}_{CO \cdot C \cdot CH_2 \cdot CH_2 \cdot CO_2H}$, are obtained. On reduction by means of hydrogen iodide in acetic acid and phosphonium iodide, the same products were obtained as are given by hæmin, including hæmopyrrole and phonopyrrolecarboxylic acid. Mesoporphyrin is considered to be a simple reduction product of hæmin minus its iron. Possibly the porphyrin spectrum is due to the elimination of the complex iron grouping from hæmin; in fact, the complex iron salt of porphyrin shows the hæmin spectrum. It is probable that two alcoholic hydroxyl groups are reduced in the formation of mesoporphyrin.

Pure mesoporphyrin has no poisonous photobiological action, whereas hæmatoporphyrin when injected subcutaneously into mice which are exposed to light causes death.   E. F. A.

[**Guanylic Acid.**] IVAR BANG (*Biochem. Zeitsch.*, 1912, 46, 500—501).—The author believes that the guanylic acid recently isolated in the form of a crystalline brucine salt by Levene and Jacobs (A., 1912, i, 926) is not guanylic acid itself, but a scission product.
                                                                   S. B. S.

The Pentose of Guanylic Acid. KG. O. AF KLERCKER (*Biochem. Zeitsch.*, 1912, 47, 331—342).—The author gives a general view of the literature concerning the sugar derived from the pancreatic nucleic acid, guanylic acid, and allied substances. He prepared the osazone from guanylic acid, and obtained rotations of -0.59 to $-0.64°$ for 0.2 gram in 10 c.c. for various preparations recrystallised from alcohol. For *l*-arabinose preparations obtained in the same way he obtained numbers from $+0.62$ to $0.69°$, and for *l*-xylose preparations -0.67 and $0.70°$. The sugar from which the guanylic acid pentosazone was prepared was lævorotatory, and as xyloses yield osazones which rotate in the opposite direction to the sugars themselves, the conclusion is drawn that the guanylic acid pentose is not *l*-xylose, but probably belongs to the *d*-arabinose group. The conclusion is also supported by the general character of the osazones as regards behaviour on crystallisation and appearance. Nevertheless, the author states that the optical properties of the phenylpentosazones do not

form a satisfactory criterion for distinguishing between the various sugars.   S. B. S.

The Optimal Hydrogen-ion Concentration for the Liquefaction of Gelatin by Trypsin. SVEN PALITZSCH and L. E. WALBUM (*Biochem. Zeitsch.*, 1912, 47, 1—35).—Fermi's method was employed, but was modified in two particulars, in that, firstly, boracic acid was added to the gelatin to avoid change of hydrogen-ion concentration during the digestion, and, secondly, the digestion mixture was neutralised after completion of the action of trypsin, so that the actual cooling process took place at the same hydrogen-ion concentration, for it was found that solutions of undigested gelatin solidified more slowly in alkaline than in neutral solutions in the absence of boric acid, although there was not much difference when this acid was present. By means of this method it was found that the optimal conditions for liquefaction were at the following hydrogen-ion concentrations : at 30°, $10^{-9\cdot9}$; at 37°, $10^{-9\cdot7}$; at 45°, $10^{-9\cdot1}$; at 55°, $10^{-8\cdot0}$; that is to say, the higher the temperature, the nearer to the neutral point is the hydrogen-ion concentration for tryptic activity when measured by the Fermi process.   S. B. S.

The Mechanism of Pepsin Digestion. JOHANNE CHRISTIANSEN (*Biochem. Zeitsch.*, 1912, 47, 226—249).—The viscometric method was adopted, and in the preliminary experiments on the action of acid on genuine proteins (dialysed serum proteins, etc.), it was found that the addition of acid increased the viscosity of the solutions up to a certain maximum point, after which further additions caused a diminution. The Günzburg reaction for hydrochloric acid becomes positive at the point of maximal viscosity, thus bearing out Pauli's theory that at this point the solution contains essentially chlorine ions and heavily hydrated protein ions. The viscosity is diminished by filtration through paper, more especially when only just sufficient acid is present to produce the maximum readings. With larger excess of acid, the effect of filtration becomes less marked. Similar results were obtained on filtration of mixtures of protein and alkali, and the results indicate that the protein ion is adsorbed by the paper. In investigating the action of pepsin, viscosity changes of mixtures having the same initial viscosity but different amounts of acid (that is, amounts of acid less and more than necessary to produce a mixture with the maximum viscosity) were chosen. It was found that such corresponding mixtures, under the influence of pepsin, changed their viscosities at the same rate, which fact seems to indicate that in the neighbourhood of maximal viscosity the rate of pepsin action is independent of the hydrogen-ion concentration. This result is not in accordance with results obtained with coagulated egg-white, which requires a certain excess of acid for maximal digestion rate. The difference is ascribed to the change in the character of the protein. Preliminary experiments carried out with dialysed sheep serum-albumin, in which the rate of formation of acid albumin was ascertained (this is only formed in this case when pepsin is present as well as acid), also indicated that the maximum rate of formation of this product takes place at the

point of maximum viscosity (that is, when there are the maximum number of protein ions present). S. B. S.

The Enzymes of the Pancreas. I. The Generation of Trypsin from Trypsinogen by Enterokinase. JOHN MELLANBY and V. J. WOOLLEY (*J. Physiol.*, 1912, 45, 370—388).—The time occupied in activating trypsinogen by enterokinase is a function of the amount of the latter enzyme added. As the action proceeds, trypsin is produced at a constantly increasing rate. The reaction is accelerated by rise of temperature ; it occurs best in a neutral medium, is delayed by alkali, and stopped by acid. There is no evidence that trypsin can activate trypsinogen, or that trypsin acts as a co-enzyme to enterokinase. Proteins apparently delay activation, because the trypsin first formed is adsorbed by the protein ; the delay varies in different proteins. The following theory is advanced : Enterokinase is a proteolytic enzyme acting best in a neutral medium ; trypsinogen contains a protein moiety with which trypsin is combined, and in this combination the proteolytic properties of trypsin are masked. The generation of trypsin from trypsinogen by enterokinase depends on the adsorption of the enterokinase by the protein moiety of the trypsinogen ; digestion of the protein moiety follows, and trypsin is thus liberated. W. D. H.

Action of Hydrogen Chloride on Invertase. II. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1912, 82, 377—390. Compare following abstract).—Purified invertase takes up considerable quantities of hydrogen chloride, losing its specific activity. The greater part of the hydrogen chloride is removed on keeping in a vacuum, but the hydrolytic activity is not regained.

The invertase preparation contained 5·57% of nitrogen, 2·3% being amide nitrogen and 3·17% titratable in presence of formaldehyde. The ash amounted to 22·2% ; the acidity was five to six times as large as in the case of purified diastase.

The destruction of the enzymic activity is not due to the formation of salts with the basic or other atomic groups of the enzyme, but the action of the acid reduces the amount of nitrogen which can be titrated in presence of formaldehyde, pointing to the formation of condensation products between the carboxyl and amino-groups.

The active component of invertase accordingly possesses a different constitution from that of diastase. E. F. A.

Action of Hydrogen Chloride on Diastase. I. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1912, 82, 276—325).—When dry hydrogen chloride is passed over purified diastase the enzyme takes up a good deal of the gas, forming with it a loose chemical compound ; the enzyme loses its specific activity. On exposure in a vacuum the hydrogen chloride is removed and the activity of the enzyme restored. It is shown that the hydrogen chloride is not fixed to the amide or secondary nitrogen atoms of the enzyme complex, and that only part is attached to the basic groups. The action of the acid does not cause any particular hydrolysis of the enzyme molecule. The specific

enzyme action of diastase is due to the atomic groups which can fix hydrogen chloride.   E. F. A.

Malt Diastase, and the Action of Potassium Phosphates on It. RUTGER C:SON HEYL (*J. pr. Chem.*, 1912, [ii], **86**, 433—457). —The author has studied the diastatic hydrolysis of starch under various conditions by determining the amount of maltose produced, according to Bertrand's method (A., 1907, ii, 136).

In the first part of its course, the diastatic actions follow the logarithmic curve, and in such a manner as if only a part of the starch were capable of hydrolysis.

The magnitude of this part depends on the concentration of the starch and of the enzyme, and also on the presence of electrolytes and proteins. In the last part of its course, the reaction proceeds with extreme slowness.

Potassium dihydrogen phosphate exercises an activating influence on the enzyme, and the same is true with respect to the action of dipotassium hydrogen phosphate on old solutions of the enzyme; in freshly prepared solutions the latter salt exerts a retarding influence.

The activating action of the phosphates is considerably influenced by the presence of proteins in the enzyme solutions.   F. B.

Reaction between Enzymes and Other Substances. SVEN G. HEDIN (*Zeitsch. physiol. Chem.*, 1912, **82**, 175—178).—Introductory to following paper.   W. D. H.

The Action of Certain Colloids on the Inhibition of Enzyme-actions. G. JAHNSON-BLOHM (*Zeitsch. physiol. Chem.*, 1912, **82**, 178—208).—Saponin completely hinders the inhibitory effect of charcoal on rennet, and partly that of normal serum. The saponin appears to liberate the enzyme which is adsorbed by the charcoal, and the reaction is a rapid one. It is accelerated by elevation of temperature, and by increase in the amount of saponin. Saponin increases the inhibitory effect of immune serum on rennet. Saponin partly activates a solution of rennet-zymogen. It acts similarly on trypsin adsorbed by charcoal, but has no effect on the antitryptic action of serum-albumin. Cholesterol acts like saponin on charcoal and rennet, but increases the inhibitory effect of normal serum. It has no influence on the antitryptic action of charcoal and serum-albumin. Egg-white if treated with hydrochloric acid and neutralised, partly inhibits the anti-rennetic power of normal serum. W. D. H.

The Coagulation of Milk by Rennet. JOHN MELLANBY (*J. Physiol.*, 1912, **45**, 345—362).—The clotting of milk by pancreatic rennet follows the same general laws as that by gastric rennet, but the two enzymes are distinct, because they differ in the effect of alkali on them; their anti-enzymes in serum are specific, and pancreatic rennet requires a greater amount of calcium than gastric rennet does. In the case of both enzymes, calcium salts may be replaced by salts of barium, strontium, or magnesium. There is no indication from electrical conductivity determinations that calcium enters into chemical com-

bination during the curdling process. The hypothesis is advanced that all proteolytic enzymes curdle milk, provided suitable conditions are provided; those, like pepsin, which act best in an acid medium requiring less calcium than those which, like trypsin, act in a alkaline medium. The coagulation of milk is due to the adsorption of the enzyme by the caseinogen, and the enzyme-caseinogen complex is precipitated by the bivalent calcium ions of the milk; the quantity of ionised calcium salt required to effect precipitation is intimately related to the quantity of enzyme adsorbed. A method based on this hypothesis is described for the detection and estimation of proteolytic enzymes. W. D. H.

The Biochemical Rôle of Peroxydases in the Transformation of Orcinol into Orcein. JULES WOLFF (*Compt. rend.*, 1912, 155, 1031—1032. Compare A., 1912, i, 928).—The action of ammonia and atmospheric oxygen on orcinol in dilute solutions is a very slow oxidation, this being the first condition for the formation of orcein. The introduction of a peroxydase influences far more the formation of the colouring matter than the amount of oxygen absorbed. W. G.

The Nomenclature of the Polyphenoloxydases. FR BATELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1912, 46, 395—396).—The authors recommend the term *polyphenoloxydase* to indicate an enzyme which accelerates the oxidation of polyphenols and the corresponding amino-derivatives. Such ferments are to be distinguished from those of the character of tyrosinase, which acts similarly on monophenols, and which are designated simply *phenoloxydases*. The expression phenolase is to be avoided in this sense, as it indicates a ferment which accelerates the hydrolysis of an aromatic ester. S. B. S.

Preparation of Organic Arsenic Compounds. HEINRICH BART (D.R.-P. 250264. Compare La Costa and Michaelis, A., 1880, 396; Schraube and Schmitt, A., 1894, i, 237).—The following organic arsenic compounds have been obtained by treating diazotised solutions of the following bases with sodium arsenite and subsequently heating in the presence of sodium hydroxide until the evolution of nitrogen ceases. p-*Bromophenylarsinic acid* (colourless needles) from p-bromoaniline; o-*benzoarsinic acid* (colourless needles) from o aminobenzoic acid; p-*acetylaminophenylarsinic acid* from monoacetyl-p-phenylenediamine; p-tolylarsinic acid (Abstr., 1880, 396) from p-toluidine: and *compounds* from potassium *iso*diazobenzene and o-nitro*iso*diazobenzene; from 4-nitro-2-aminophenol; from p-nitroaniline (which is best decomposed in tartaric or oxalic acid solutions), and from the same base decomposed in the presence of sodium p-nitrophenylarsenite; whilst p-aminophenylarsinic acid furnishes *benzene*-p-*diarsinic acid.*

The *sodium* salts of these compounds are colourless or grey needles, and the original contains numerous formulæ illustrating possible phases in their formation. F. M. G. M.

Preparation of Derivatives of 3:3'-Diamino-4:4'-dihydroxy-arsenobenzene. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 250745).—When 3:3'-diamino-4:4'-hydroxyarsenobenzene is treated with halogenated acetic acid (or its homologues) in aqueous alkaline solution it yields neutral, soluble compounds of therapeutic value.

The *compound*, $NH_2 \cdot C_6H_3(OH) \cdot As \vdots As \cdot C_6H_3(OH) \cdot NH \cdot CH_2 \cdot CO_2H$, is obtained when 3:3'-diamino-4:4'-dihydroxyarsenobenzene (100 parts), dissolved in a mixture of methyl alcohol (300 parts), and water (300 parts) containing sodium hydroxide (4 mols.), is treated with chloroacetic acid (50 parts) and potassium iodide (36 parts) and heated at 60—65° during two to three hours in an indifferent gas with exclusion of air ; the product is isolated by the limited addition of acid. The brownish-yellow *sodium* salt is precipitable with alcohol; the *potassium* and *ammonium* salts forms similar powders.

The *compound*, $NH_2 \cdot C_6H_3(OH) \cdot As \vdots As \cdot C_6H_3(OH) \cdot NH \cdot CHMe \cdot CO_2H$, a yellow powder, is prepared in a similar manner with α-bromo-propionic acid, and furnishes *alkali* salts, whilst *diaminodihydroxy-arsenobenzenediacetic acid*, $As_2[C_6H_4(OH) \cdot NH \cdot CH_2 \cdot CO_2H]_2$, is obtained with bromoacetic acid.   F. M. G. M.

Preparation of Unsymmetrical Aromatic Arseno-compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 251104).—When an equimolecular mixture of two arylarsinic acids (or oxides) is reduced it yields an unsymmetrical aromatic arseno-compound.

3:4'-*Diamino-4-hydroxyarsenobenzene hydrochloride* (annexed formula), a yellow, microcrystalline powder,

HCl, NH_2 ⬡ $\cdot As \vdots As \cdot$ ⬡ NH_2, HCl / OH

is obtained as follows : *p*-Amino-phenylarsinic acid (21·7 parts) or its equivalent of *p*-aminophenyl-arsenious oxide (A., 1909, i, 347) and 23·3 parts of 3-amino-4-hydroxy-phenyl-1-arsinic acid (A., 1910, i, 803) in methyl alcohol (100 parts) and concentrated hydrochloric acid (39 parts) is slowly stirred into a mixture of stannous chloride (100 parts) dissolved in alcohol (300 parts) to which has been added 500 parts of alcohol saturated with hydrogen chloride and 17 parts of hydriodic acid (D 1·7), the temperature meanwhile being maintained at −5° to −10°, the product is slowly precipitated in crystalline form. The *sulphate* forms a flocculent, yellow insoluble precipitate.

Phenylglycylarsenious chloride, $AsCl_2 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO_2H, HCl$, a crystalline paste which can be washed with acetic acid and ether, is prepared by reducing a concentrated hydrochloric acid solution of phenylglycylarsinic acid (to which a trace of hydriodic acid has been added) with sulphurous acid at −10° ; it is decomposed readily by alkalis to the corresponding hydroxide.

3-*Amino-4-hydroxy-4'-glycylarsenobenzene* (annexed formula) is obtained as a viscous, yellow paste when molecular proportions of the foregoing chloride and 3-amino-4-hydroxyphenyl-

$CO_2H \cdot CH_2 \cdot NH$ ⬡ $\cdot As \vdots As \cdot$ ⬡ NH_2 / OH
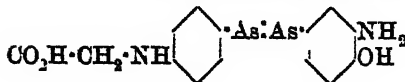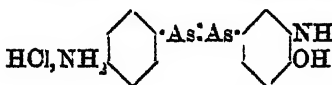
arsenious oxide (A., 1911, i, 1055) in methyl-alcoholic solution are reduced with sodium hyposulphite at the ordinary temperature.

3': 5'-*Dichloro-3-amino*-4 : 4'-*dihydroxyarsenobenzene*, a yellow powder, is prepared from 3-amino-4-hydroxyarsenious oxide and 3 : 5-*dichloro-4-hydroxyphenylarsenious oxide*, $AsO \cdot C_6H_2Cl_2 \cdot OH$, which latter compound is obtained by the reduction of dichloro-*p*-hydroxyphenylarsinic acid (*loc. cit.*); 3-*amino-4-hydroxyarsenobenzene*, $C_6H_5 \cdot As_2 \cdot C_6H_3(NH_2) \cdot OH$, a fawn-yellow powder, is prepared from phenylarsenious oxide and 3-amino-4-hydroxyphenylarsenious oxide. F. M. G. M.

Preparation of Products Reduced Beyond the Arseno-stage from Substituted Aromatic Arsinic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 251571).—It is found that when powerful reducing agents (such as tin, zinc, or iron) in concentrated acid solution act on arylarsinic acids that they can be reduced beyond the arseno-condition (compare Palmer and Dehn, A., 1902, i, 86).

The following *compounds* are described :

(1) From *p*-hydroxyphenylarsinic acid as a colourless precipitate, soluble in alkalis, and isolated by means of carbon dioxide; it darkens at 75° and decomposes violently at 155°.

(2) From *p*-aminophenylarsinic acid, a colourless oil, b. p. 132°/ 10 mm., which exposed to air is rapidly converted into diaminoarsenobenzene.

(3) From phenylglycylarsinic acid, a colourless precipitate which rapidly darkens, and is isolated in the form of its *zinc* salt.

(4) From 3-nitro-4-hydroxyphenylarsinic acid (A., 1910, i, 803), isolated as its *zinc* salt; the free *arsine* is a colourless powder darkening at 100° and decomposing violently at 135°.

F. M. G. M.

Formation of Organo-metallic Compounds during Electrolytic Reductions. JULIUS TAFEL (*Ber.*, 1912, 45, 3321).—Polemical against Law (T., 1912, 101, 1016, 1544). A claim for priority. Law's statement that the formation of organo-metallic compounds at mercury cathodes has never been observed is incorrect (compare A., 1906, i, 941; 1911, i, 764). T. S. P.

Chemico-therapeutical Researches on Mercury Compounds. Mercuridi-*p*-aminophenol. ERNEST FOURNEAU and A. VILA (*J. Pharm. Chim.*, 1912, [vii], 6, 433—441).—p-*Nitrophenylmercuric acetate*, $C_8H_7O_5NHg$, obtained by the action of mercuric acetate on sodium *p*-nitrophenol dissolved in boiling water, crystallises in flattened, colourless needles, and on treatment with carbon dioxide furnishes the corresponding *oxide* (compare A., 1911, i, 1056). The latter by a complex series of reactions, which are discussed in detail in the original, gives with sodium sulphide, *sodium di-p-nitromercuridiphenol*, $C_{12}H_{10}O_6N_2HgNa_2$, crystallising in garnet-red needles, from which the corresponding *mercuridi-p-nitrophenol* is liberated by the action of acids. This on reduction in alkaline solution by sodium hyposulphite yields *di-p-aminomercuridiphenol*, $Hg[C_6H_3(OH)NH_2]_2$, crystallising in heavy needles, insoluble in water, but readily soluble in alcohol; the *hydrochloride* forms brilliant needles soluble in water. The free base oxidises rapidly in alkaline solution on exposure to air.

This substance is toxic, producing the ordinary symptoms of mercurial poisoning, due no doubt to the liberation of simple mercury derivatives by oxidation in the organism. The *acetyl* derivative crystallises in slender needles, is soluble in alkalis, forming stable solutions, and is much less toxic than the parent base.   T. A. H.

Preparation of Nuclear-substituted Mercury Derivatives of Polysubstituted Phenols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 250746. Compare A., 1911, i, 1056; 1912, i, 754).—Organic mercury compounds have previously been prepared (compare Dimroth, A., 1902, i, 656, and *loc. cit.*), and the following more complex derivatives are now described.

The crystalline *compound*, $OH \cdot C_6H_2Me_2 \cdot Hg \cdot OAc$, is obtained when 12 parts of *p*-xylenol (A., 1878, ii, 410) dissolved in methyl alcohol are treated with mercuric acetate (30 parts) in water (100 parts) and gently warmed until the addition of an alkaline hydroxide ceases to precipitate mercuric oxide.

Similar *compounds* from creosol, pyrogallol 1 : 3-diethyl ether (A., 1878, ii, 869), and from bromo-*p*-xylenol (A., 1878, ii, 410) are described in the original.   F. M. G. M.

Preparation of Derivatives of Aminobenzoic Acid and its Salts Containing Mercury in the Ring. VEREINIGTE CHEMISCHE WERKE AKTIENGESELLSCHAFT (D.R.-P. 249725).—When the mercury salts of *o*-, *m*- or *p*-nitrobenzoic acid are heated during some hours at about 225°, the mercury becomes attached to a ring carbon atom ; these *nitro*-compounds can then be reduced to the corresponding amines.

pp-*Diamino*-oo′-*mercuridibenzoic acid* (annexed formula), a colour-less (to yellow) crystalline powder, is obtained by reducing the nitro-compound with ferrous sulphate in alkaline solution ; the crystalline *hydrochloride* can be isolated by means of alcohol. The *barium, calcium, silver*, and *lead* salts are precipitable ; the nickel salt gives a greenish-blue, and the iron salt a brown, solution ; the green solution of the copper salt becomes brown when boiled, a characteristic which distinguishes it from the solution of the copper salt of the nitro-compound, which is blue and unaffected by boiling.

The ortho- and meta-compounds have similar reactions, and are obtained by the same method ; or the mercury salt can be replaced by other salts of aminobenzoic acids, which are then heated with a salt of mercury.   F. M. G. M.

Preparation of Dinitrodiphenylmercuridicarboxylic Acids. VEREINIGTE CHEMISCHE WERKE AKTIEN GESELLSCHAFT (D.R.-P. 251332. Compare preceding abstract).—A further account of the preparation of *pp*-dinitro-*oo′*-mercuridibenzoic acid, in which a catalyst, such as stannous chloride or ferrous hydroxide, is employed to assist the condensation ; together with the preparation and properties of the *sodium, silver, barium, nickel*, and *cobalt* salts.
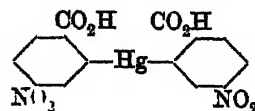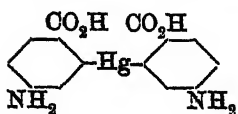
mm'-Dinitro-*oo'*-mercuridibenzoic acid and its *sodium, silver, barium, nickel,* and *iron* salts are also described ; the salts of these compounds are extremely poisonous, and possess a powerful therapeutic action. F. M. G. M.

Preparation of Esters of Aromatic Carboxylic Acids containing Mercury and their Products of Hydrolysis. WALTER SCHOELLER and WALTHER SCHRAUTH (D.R.-P. 248291. Compare A., 1912, i, 754).—When glycyl salicylate (182 parts) and mercuric acetate (318 parts) are boiled together during several hours in methyl-alcoholic solution, a crystalline *ester*, m. p. 165—170° and containing 45·5% Hg, is obtained, which, on hydrolysis, furnishes a compound identical with "hydrargyrum salicylicum." Methyl anthranilate (165 parts) under similar conditions furnishes a *product*, m. p. 191°, containing 47·28% Hg, and on hydrolysis an inner *anhydride* containing 57·3% mercury ; whilst *iso*butyl *p*-aminobenzoate yields a *compound*, m. p. 208° (decomp.), with mercury content 44·24%, and an *anhydride* containing 59·51% Hg.

The *phenyl glycyl* ester has m. p. 128—131°, contains 45·9% Hg, and the corresponding *anhydride* has 57·3% Hg. F. M. G. M.

Physiological Chemistry.

The Regulation of Neutrality by the Respiratory Centre, and its Stimulability in Maintaining the Carbon Dioxide Tension of the Blood. KARL A. HASSELBALCH (*Biochem. Zeitsch.*, 1912, 46, 403—439).—The conception underlying these investigations is the following : The magnitude of the lung ventilation is regulated by the magnitude of the stimulus and the stimulability of the breathing centre. The stimulus is the excess of the hydrogen-ion concentration above normal of the blood. A given magnitude of stimulus will cause a greater ventilation of the lungs the greater the stimulability of the centre, and vice versa. The C_H of the blood will alter therefore in the inverse ratio to the stimulability of the centre. This theory was tested in the following way : Considerable changes in the C_H of the urine were brought about on normal individuals by changes in the diet. The magnitude of the changes thus caused were greater than deviations from the normal found in pathological urine. The effect of such a change was to cause a change in the tension of the alveolar carbon dioxide in an opposite direction. It was experimentally shown, furthermore, that the changes in diet did not affect the stimulability of the centre. This fact was ascertained by measuring the effect on the respiration of breathing increased quantities of carbon dioxide. It was further found that the C_H of the blood (measured under a constant carbon dioxide tension) altered under varying conditions of diet, in the

same direction as the C_{H} of the urine. The alveolar carbon dioxide tension appears to alter in such a way that the actual C_{H} of arterial blood (measured under the same carbon dioxide tension as exists in the arteries) remains a constant under the varying conditions. The theory is supported by experiments in which the stimulability of the centre was artifically diminished (as, for example, by morphine) or increased.   S. B. S.

Absence of Apnœa After Forced Breathing. WALTER M. BOOTHBY (*J. Physiol.*, 1912, **45**, 328—337).—In some persons, forced breathing is not followed by apnœa; the loss of carbon dioxide consequent on forced breathing is made up within a few minutes, but not so rapidly as when apnœa occurs. This exceptional condition is probably due to a compensating diminution of the circulation through the respiratory centre, in consequence of which the gas tensions in the centre are still capable of exciting it.   W. D. H.

The Differences in Composition between Arterial and Venous Blood. HUGO WIENER (*Zeitsch. physiol. Chem.*, 1912, **82**, 243—265).—The total protein in the blood of the renal vein is less than in that of the carotid artery and femoral vein (dog). Venous blood is relatively rich in globulin, but this is not so marked in the blood of the renal vein. In nephritis, the reverse obtains.
                                                         W. D. H.

Distribution of Sodium and Potassium in the Animal Organism. P. J. GÉRARD (*Chem. Zentr.*, 1912, ii, 846—847; from *Bull. Sci. pharm.*, 1912, **19**, 265—283).—In three successive venesections. the ratio K : Na in rabbit's blood varied between 0·68 and 0·61. The sodium in contrast to the potassium remained constant, deficiences of the former being replaced by sodium withdrawn from the tissues. The ratio was also determined in various marine and land animals, and in various secretions. The author, when working with mice and frogs, was unable to confirm the antagonistic action of sodium salts on the toxic action of potassium salts, as demonstrated by Loeb in the case of *Fundulus*. The toxic action of potassium depends to a large extent on the concentration of the solution employed.   S. B. S.

The Influence of Nitrogenous Metabolism Products which Occur Naturally in Blood and Urine on the Blood Pressure. E. LOUIS BACKMAN (*Chem. Zentr.*, 1912, ii, 624; from *Zentr. Physiol.*, 1912, **26**, 166—169).—Urea in from 2—10% solutions in saline caused a rise of blood-pressure (maximum 26 mm. mercury) when injected into rabbits. Ammonium carbamate in 0·5% solution caused a lasting rise, whereas in 0·1% solution it exerted no action. Ammonium carbonate in 0·6% solution caused a lowering of blood-pressure (maximum 38 mm.), but in 0·1% solution a lasting rise. Six °₀ ammonium hippurate caused a transient rise (9 mm.), followed by a lowering. Three % solutions caused a slight rise. Creatine, hypoxanthine, and sodium urate caused lasting rises. Allantoin in

2% solution caused a lasting rise (maximum 5 mm.), and in 1% also a rise after a considerable latent period. Urea also exerts an influence on the heart beats. A mixture of 2% urea, 0·05% ammonium carbamate, 1% sodium hippurate, 1% creatine, 0 2% hypoxanthine, 0·01% xanthine, 0·03% sodium urate causes a large (maximum 46 mm.) and long lasting rise, but has small influence on the frequency of the heart beat. The investigations indicate that nitrogenous metabolism products exert an autoregulatory function in the organism, and their action explains certain pathological conditions in gout and nephritis.

S. B. S.

The Part Played by the Suprarenals in the Normal Vascular Reactions of the Body. G. von ANREP (*J. Physiol.*, 1912, 45, 307—317).—Stimulation of the splanchnic nerves causes a rise of blood-pressure, which occurs in two phases. The second phase is accompanied by constriction of peripheral blood-vessels (even after denervation) and by increased cardiac activity (also after denervation). This second rise is due to discharge of adrenaline into the circulation, and is absent after extirpation of the two suprarenal glands.

W. D. H.

Local Vascular Reactions and their Interpretation. G. von ANREP (*J. Physiol.*, 1912, 45, 318—327).—The contraction of blood-vessels, described by Bayliss as a local reaction of the vessel wall to increased internal pressure, is due to the action of adrenaline, the secretion of which is increased under the conditions of his experiments. The dilatation of blood-vessels, ascribed by Bayliss to lowering of internal pressure, is due to the direct action on the vessel walls of asphyxial products.

W. D. H.

Glycolysis. III. The Influence of Glycine and Boric Acid Anions on the Oxidative Destruction of Dextrose in the Presence of Phosphates. WALTHER LÖB and S. GUTMANN (*Biochem. Zeitsch.*, 1912, 46, 288—295. Compare A., 1911, ii, 504).—It has been already shown that phosphate mixture accelerates the destruction of dextrose by hydrogen peroxide. This is not due to the neutrality of the medium, but is specific for phosphates, as no acceleration takes place when neutral borate or other mixtures of the same hydrogen-ion concentration are employed. The authors now show that the addition of such a borate mixture to the phosphate mixture exerts no very marked action, whereas a similar glycine mixture (prepared according to Sörensen) exerts a marked inhibitory action on the glycolysis.

S. B. S.

The Significance of Proteolysis in Specific Hæmolysis. KOHSHI OHTA (*Biochem. Zeitsch.*, 1912, 46, 247—252).—An immune serum (sheep's blood into rabbit) hæmolyses the specific blood (of sheep) without any proteolysis.

S. B. S.

The Influence of the Hydrogen-ion Concentration on Specific Precipitin Reactions. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1912, 47, 59—72).—The forma-

tion of specific precipitins and agglutins is, within wide limits, independent of the hydrogen-ion concentration. This factor only comes into play, to any extent, when the reacting substances are in very dilute solutions. In this respect, the precipitin reaction differs from the non-specific precipitation of colloids, as no optimal conditions for precipitin reaction, analogous to the isoelectric point, could be discovered. These results indicate that there is some specific chemical affinity coming into play, and the electric charge of the particles plays only a subordinate part. S. B. S.

The Coagulation of Blood. ERNST FULD and ERICH SCHLESINGER (*Chem. Zentr.*, 1912, ii, 1569; from *Berlin klin. Woch.*, 1912, 49, 1323—1327).—Dialysis of the blood against an isosmotic salt solution deprives the plasma of its power of coagulating, the crystalloid which is removed being the calcium salt of fibrin. The absence of this salt also hinders the formation of another necessary element in coagulation, namely, the fibrin ferment, for the development of which, cytothrombin from the cells and plasmothrombin from the plasma are also necessary. The injection of cytothrombin into a vein at once causes coagulation, owing to the formation of this ferment, *neothrombin*. The smallest amounts of enzymes would soon set up fermentation processes, which would hinder the circulation, were there not also present substances which prevent coagulation.

Fibrin may be redissolved by fibrinolysis, which is partly due to salt action and also to an enzymatic agent, *thrombase*. J. C. W.

The Dissociation of Oxyhæmoglobin in Human Blood During Partial Carbon Monoxide Poisoning. J. B. S. HALDANE (*Proc. physiol. Soc.*, 1912, xxii–xxiv; *J. Physiol.*, 45).—The presence of carboxyhæmoglobin in the blood delays the dissociation of the oxyhæmoglobin present, so that even though the amount of oxyhæmoglobin may be half the normal (as it may also be in a man with anæmia without grave results), the combination of the remaining half of the hæmoglobin with carbon monoxide produces a serious state of affairs. W. D. H.

Blood-relationships of Animals as Displayed in the Composition of the Serum-proteins. I. A Comparison of the Serum of the Horse, Rabbit, Rat, and Ox in the Normal and Fasting Condition. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1912, 13, 325—340).—The amounts of insoluble globulin, total globulin, and total albumin in serum were determined by the author's refractometric method. In the rabbit the results agree with those arrived at by others in other ways. Horse serum yields not more than 40% of the total albumin in crystalline form. In fully fed animals the three groups of proteins vary greatly; but the average values are characteristic of the species. In fasting, the total protein is also highly variable; in starvation it rises. In rabbit, ox, and horse, inanition increases the relative amount of albumin, whereas in rat and dog the reverse obtains. W. D. H.

The Diastatic Action of Human Saliva. GOICHI HIRATA (*Biochem. Zeitsch.*, 1912, 47, 167—183).—The diastatic value of saliva (as determined by Wohlgemuth's method) remains practically constant throughout the day, and is not influenced by the time of meals or the diet. The value is also independent of the amount of saliva secreted, and of the age or sex of the individual. It has the same value in certain pathological cases investigated as in normal cases, and appears to be uninfluenced by the hæmoglobin content of the blood. In the case of the Japanese, it varies between D_{50}^{35} 160 and 640 in different individuals. S. B. S.

Formation of Hydrochloric Acid in the Stomach. J. LÓPEZ-SUÁREZ (*Biochem. Zeitsch.*, 1912, 46, 490—499).—The author discusses the evidence as to the acid-secreting function of the oxyntic cells of the stomach, and considers that this has not been demonstrated. By direct chemical analysis he shows that the mucous membrane of the fundus contains more chlorine than that of the pylorus. He shows, furthermore, by Macallum's histological method that the ordinary cells contain more chlorine than the oxyntic cells. S. B. S.

The Fat-hydrolysing Ferment in Gastric Juice, and its Estimation. HEINRICH DAVIDSOHN (*Chem. Zentr.*, 1912, ii, 1378—1379; from *Berl. klin. Woch.*, 1912, 49, 1132—1134).—Rona and Michaelis's drop method for following the course of butyrin hydrolysis (A., 1911, ii, 302) has been applied to a large number of gastric juices, and a widely varying enzyme action has been observed. Directions are given whereby the method may be applied to the estimation of this hydrolytic enzyme. J. C. W.

Tryptic Digestion of Cynoscion regalis. GEORGE F. WHITE and ADRIAN THOMAS (*J. Biol. Chem.*, 1912, 13, 111—116).—The flesh of *Cynoscion regalis*, an American fish known commonly as the weakfish or squeteague, was subjected to tryptic digestion in vitro, and the amino-acids in the digest were determined by Sörensen's formaldehyde method. The results were regular and in accord with those obtained by van Slyke's nitrous acid method for estimating amino-nitrogen. The relatively low rate at which the protein becomes soluble agrees with the results of metabolism experiments. Very low cleavage products are formed as soon as the protein passes into solution, the average size of the peptides being 2·02 after half an hour's digestion; but there is a very stable nitrogen complex which is not attacked by trypsin. W. D. H.

Animal Calorimetry. V. The Influence of the Ingestion of Amino-acids on Metabolism. GRAHAM LUSK and J. A. RICHE (*J. Biol. Chem.*, 1912, 13, 155—184. Compare A., 1912, ii, 1189).—After giving meat, the metabolism of the dog during the second hour rose almost to a maximum, and the respiratory quotient was 0·9; it therefore appears that carbohydrate and not additional protein is oxidised during this period. After the ingestion of amino-acids and especially of glycine, there is a similar increase in the metabolism;

this can have nothing to do with deamidation or urea-formation, but is attributed to a direct stimulating action of the amino-acids on the cells of the body.   A mixture of five amino-acids produced a more rapid metabolism than when given singly, and more than meat containing the same amount of nitrogen.   W. D. H.

Animal Calorimetry. VI. The Influence of Mixtures of Food-stuffs on Metabolism. GRAHAM LUSK and J. A. RICHE (*J. Biol. Chem.*, 1912, 13, 185—208).—Further details are given of the effect of diet on metabolism, and the conception of the process put forward is that to a basal metabolism (at rest) there may be added metabolism due to plethora, that is, an increased supply of fats and carbohydrates, or the superadded metabolism may be due to the stimulus of amino-acids.   When these two are added to each other there is no summation of effects.   W. D. H.

Fatty Acid Metabolism in the Liver. II. The Relation of the Fatty Acids in the Food of the Plaice to those in their Livers and Myotomes. V. H. MOTTRAM (*J. Physiol.*, 1912, 45, 363—369).—The fatty acids of the mussel have a high iodine value, which falls between that of the fatty acids of the liver and those of the myotomes of the plaice.   Such fatty acids are therefore not characteristic of the vertebrates, and they occur before the appearance of a true liver.   Their formation is not exclusively a liver function.   The experiments on the feeding of plaice on mussels cannot, however, be considered a refutation of Leathes' theory of the desaturating influence of the liver in fatty acid metabolism.   W. D. H.

The Biochemical Synthesis of Fatty Acids from Carbohydrates. IDA SMEDLEY (*Proc. physiol. Soc.*, 1912, xxv—xxvii; *J. Physiol.*, 45).—Various hypotheses to explain the conversion of carbohydrate into fat are discussed.   Although pyruvic and other α-keto-acids have not yet been detected in the tissues, the theory is favoured that pyruvic acid is an intermediate product.   W. D. H.

Maintenance Experiments with Isolated Proteins. THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, and EDNA L. FERRY (*J. Biol. Chem*, 1912, 13, 233—276).—Details are given and general questions discussed on the nutrition of white rats for long periods on foods containing a single purified protein.   With the precautions described this is possible, and they can be so maintained for periods equal to their adult lives.   This is true for gliadin, edestin, and casein, which are proteins of very different composition.   As glycine is absent from casein, lysine and glycine from gliadin, and phosphoproteins from gliadin and edestin, and purines throughout are practically absent, the synthetic activities of the animal body are clearly brought to mind.   The possibilities of transmutation of amino-acids must be considered, and the view that proteins as near as possible in constitution to those in an animal's body are most nutritious must be regarded with caution.   Long-continued experiments are necessary in all such work. Changes in the nitrogen balance over short periods may be entirely deceptive.   W. D. H.

The Influence of Lecithin on the Nitrogen and Phosphorus Balance. ALDO PATTA (*Chem. Zentr.*, 1912, ii, 939—940 ; from *Arch. Farm. sperim.*, 1912, 13, 515—528).—Small quantities of lecithin (0·05 to 0·10 gram) administered subcutaneously to a dog scarcely altered the nitrogen and phosphorus metabolism when there was a small deficit in these substances. Larger doses (0·5 to 0·75 gram) caused a sparing action, which was small when the nitrogen and phosphorus ingested were insufficient, but was marked when these elements were in excess of the body needs. The sparing action of the phosphorus was larger than the amount injected as lecithin, and the fact that the injection caused an increase of the nitrogen in the urine, at the expense of the fœcal nitrogen, indicates that the lecithin stimulates the degradation of the injested proteins.　　　　S. B. S.

Retention of Nitrogen after Feeding on Ammonium Salts. E. GRAFE (*Zeitsch. physiol. Chem.*, 1912, 82, 347—376).—The present experiments on pigs confirm those previously recorded on dogs (A., 1912, ii, 659). Administration of ammonium salts mixed with abundance of carbohydrate leads to nitrogenous equilibrium, or even a retention of nitrogen.　　　　W. D. H.

The Creatine Metabolism of the Growing Pig. ELMER V. MCCOLLUM and H. STEENBOCK (*J. Biol. Chem.*, 1912, 13, 209—218).— In some animals (for instance, the rabbit) fasting causes the appearance of creatine in the urine. In dogs, depletion of the liver of glycogen leads to the same result, and Mendel and Rose (A., 1911, ii, 1002, 1007) consider that there is a definite relationship between creatine and carbohydrate metabolism ; they further think that creatine is not a result of exogenous protein metabolism, but only of endogenous metabolism. The present experiments on pigs were planned to investigate this question, but it was found that in this animal fasting does not lead to the appearance of creatine in the urine ; this is explained in differences of metabolic habit. When a rabbit fasts the total nitrogen excreted rises, indicating an increase of protein katabolism. This does not happen in the dog, or only slightly, and not at all in the pig. The pig is an efficient fat-storer, so he might be expected to use it readily for energy production. On an uniform diet considerable irregularities in the excretion of creatine occur, and the idea that creatine is destroyed by enzymes is supported. Data are also given which leave but little doubt that creatine may arise from exogenous as well as from endogenous protein metabolism, and that its source, or one of its sources, is arginine, is regarded as probable.　　　　W. D. H.

The Behaviour of Some Hydantoin Derivatives in Metabolism. I. Hydantoin and Ethyl Hydantoate. HOWARD B. LEWIS (*J. Biol. Chem.*, 1912, 13, 347—356).—After hydantoin is given, an insoluble benzylidenehydantoin can be recovered from the urine, which accounts for only part of the hydantoin administered. No toxic effects follow, which is against Lusini's theory of the toxicity of $\begin{smallmatrix} -HN \\ -HN \end{smallmatrix}{>}C{:}O$ groups.

Hydantoic acid, of which hydantoin is the cyclic anhydride, is not destroyed in metabolism when given as the ethyl ester. The hydantoin nucleus is not destroyed in the body of cat, rabbit or dog.

W. D. H.

Purine Metabolism. X. The Property of the Organism to Destroy, or Form by Oxidative Processes, Uric Acid in Animals Capable of Producing this Acid Synthetically. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1912, **47**, 215—225).—In experiments carried out with ducks, it was found that animals which normally synthesise uric acid can also destroy this acid after ingestion when added to a normal diet, to the extent of 33—59% of the total. They can also degrade guanine to xanthine, and into still simpler complexes which no longer contain a purine group. From the xanthine thus formed, a certain amount of uric acid can be formed by an oxidative process. Ingestion of nucleic acid also causes a slight increase in the amount of purine bases excreted and a considerable increase in the uric acid, the origin of which is ascribed to the protein groups.

S. B. S.

The Metabolism of Endogenous and Exogenous Purines in the Monkey. ANDREW HUNTER and MAURICE H. GIVENS (*J. Biol. Chem.*, 1912, **13**, 371—388).—In the urine of the guenon monkey (*Cercopithecus*), allantoin accounts for 75% of the nitrogen arising from the katabolism of endogenous purines. The rest appears principally as purine bases, uric acid being practically absent on a purine-free diet. Allantoin is a true end-product. When purines are given, allantoin is increased, and uric acid appears as an intermediate product. Only 12—54% of total purine intake is accounted for. The deficit is probably due to decomposition prior to absorption. There is no approach in this monkey to the human type of nuclein metabolism.

W. D. H.

Absorption from the Stomach. OTTO FOLIN and HARRY LYMAN (*J. Biol. Chem.*, 1912, **13**, 389—391).—A reply to London's recent criticisms (A., 1912, ii, 1189).

W. D. H.

Behaviour of Intestinal Wall After a Prolonged Period of Functional Inactivity. PAOLO MARICONDA (*Zeitsch. physiol. Chem.*, 1912, **82**, 406—412).—After making a Vella fistula, a dog was kept for several months so that no local stimulus had reached the intestine. The amount of fluid secreted by the intestinal wall was now very small, and the amount of the various enzymes was also reduced, although not to the same extent. The results are opposed to the theory that the secretory function of the intestine is due to chemical stimuli carried to it by the blood. Sucrose introduced into the fistula passes the wall without being changed; the selective absorptive power of the intestinal wall has been destroyed.

E. F. A.

Absorption of Cholic Acid in the Dog's Intestine. BAREND C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1912, **82**, 342—345).—Experiments with intestinal loops showed that in all probability cholic acid is absorbed unchanged by the intestinal wall.

W. D. H.

The Fate of Deeply-degraded Proteins in the Intestine. PETER RONA (*Biochem. Zeitsch.*, 1912, 46, 307—316).—Experiments were carried out with the object of ascertaining whether any protein synthesis takes place in the small intestine. Pieces of surviving intestine were placed in Tyrode's solution and various digestion products or mixtures of amino-acids were placed either in the solution in which the intestine was kept or introduced directly into the lumen. The experiments were carried out at 38°, and during this time the intestine maintained its peristaltic movements. The amino-nitrogen was estimated both before and after the experiment. There was generally an increase in this nitrogen at the end, due probably to amino-substances given up by the intestine itself. The amount of increase was of the same order as that in which the experiments were carried out in Tyrode's solution without any addition. No evidence was obtained therefore of any synthetical process affecting amino-derivatives in the intestine.   S. B. S.

The Investigation of the Permeability and Antagonistic Action of Electrolytes by means of a New Method. JACQUES LOEB (*Biochem. Zeitsch.*, 1912, 47, 127—166).—It has been already repeatedly shown by the author, in experiments on *Fundulus* eggs, that treatment with a solution of one salt alone (for example, sodium chloride) alters the permeability of the membrane, and that this alteration can be inhibited by the addition of certain quantities of another salt (calcium chloride). Salt solutions, of such composition that the antagonistic action of the salts is at its maximum, are designated equilibrated solutions. If fertilised eggs of *Fundulus* be brought into a solution of 50 c.c. $3M$-sodium chloride + 2 c.c. $10/8M$-calcium chloride, they will remain on the surface for three days, after which the membrane will be rendered permeable by the hypertonic solution; the eggs will then begin to shrink, and owing to the passage outwards of water, the specific gravity will increase and they will then sink in the solution. If brought into a solution of $3M$-sodium chloride alone, without presence of calcium chloride, they will sink within three to four hours, and the membrane rapidly becomes permeable. Similar phenomena are observed when the eggs are brought into other corresponding solutions containing only salts. By the method of experiment the various earlier investigations of the author have been confirmed. The changes in the permeability appear to be due chiefly to the proteins, and there is an antagonism between the action of acids and the corresponding salts, which is characteristic of proteins, as Pauli and his pupils have shown. Furthermore, the antagonism in the system H_2SO_4–Na_2SO_4 is more complete than in the system HCl–NaCl. The antagonistic action of these acids and salts on the *Fundulus* egg, as studied by the method described above, confirms the theory as to the alterations of the proteins by salts. The quantitative study of the action of alcohols, however, indicates that these alter the permeability by the action on the fatty constituents of the membrane. Provided that the action has not gone too far, the change of permeability produced by salts is a reversible one, and eggs, which have been a short time in a toxic

solution, will recover their normal properties when brought into an equilibrated solution. Eggs will also remain alive in distilled water, and fish will develop, but they will not recover their impermeability. If such eggs are brought into a solution of 50 c.c. $3M$-calcium chloride + 2 c.c. $10/8M$-calcium chloride, they sink in a few hours.

S. B. S.

The Influence of Neutral Salts on Ferment Action. II. EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1912, 47, 300—319. Compare A., 1910, i, 449).—The number of salt molecules necessary to activate to the maximum extent an inactive diastase preparation is proportional to the amount of ferment. This fact suggests a process for the determination of the quantity of ferment in a given organ. For this purpose the organ is dried, a 5% suspension of the dried powder is made up, and dialysed. The amount of salt which produces the maximum diastatic effect with this fluid can then be ascertained. By this means the diastase content in various animal organs was investigated. Organs of warm-blooded animals contain more ferment than those of the cold-blooded. The ferments obtained from both kinds of animals work more rapidly at higher temperatures.

S. B. S.

Lipoids. XVI. The Cholesterol Content of Different Parts of the Brain. SIEGMUND FRÄNKEL, P. KIRSCHBAUM, and KURT LINNERT (*Biochem. Zeitsch.*, 1912, 46, 253—256).—The cholesterol was estimated as its digitonin derivative. In a human brain 4·03% was found in the pons and medulla oblongata, 2·47% in the white matter of the cerebrum, and 1·31% in the cerebellum.

S. B. S.

The Colloidal Structure of Nerve Cells and the Changes which they Undergo. G. MARINESCO (*Zeitsch. Chem. Ind. Kolloïde,* 1912, 11, 209—225).—The ultra-microscopic structure of nerve cells is described and interpreted on the assumption that the cell constituents are of colloidal character. The structural changes which are observed, when the nerve cells are subjected to the action of acids, alkali, salts, and various other substances, such as ethyl alcohol, carbamide, glycerol, sucrose, chloral hydrate, and antipyrine, are also described in detail.

The results of these ultra-microscopic observations seem to show that the particular structures' which are presented by the nerve cells after treatment by the usual fixing and colouring methods are essentially determined by the nature of the histological processes employed. The fixing reagents have, in general, a coagulating effect on the colloidal cell constituents, and the observed facts agree with the view that the protoplasm is a negative colloid.   H. M. D.

Chemical and Biochemical Investigations on the Nervous System under Normal and Pathological Conditions IV. The Chemical Composition of the Brain in Progressive Paralysis. DOMENICO CARBONE and GIACOMO PIGHINI (*Biochem. Zeitsch.*, 1912, 46, 450—469).—The analyses of brains taken from

individuals who have suffered from progressive paralysis and Dementia præcox paraxoica were compared with those obtained from mentally normal individuals. Whereas normal brains contain about 23% of dry substance, those from mentally afflicted (five cases) varied between 17 and 21%. Against a normal value of 20%, the acetone extracts of the abnormal brains varied between 22·87% and 31·32%. The light petroleum extracts varied between 11·23% and 23·14%, as compared with the amount from normal brains of 27·84%. The cholesterol varied between 13·9 and 24·2%, and the other extractives between 4·5 and 11·84% as compared with the normal values of 10·96 and 9·64%. Full details as to analytical methods are described by the authors.   S. B. S.

Broncho-dilator Nerves. WALTER E. DIXON and FRED RANSOM (*J. Physiol.*, 1912, 45, 413—428).—The broncho-dilator nerves are of sympathetic origin. Adrenaline given to an animal showing bronchial tonus causes active temporary dilatation; atropine causes passive permanent dilatation.   W. D. H.

The Influence of Inorganic Salts on the Perfused Heart. W. BURRIDGE (*Quart. J. expt. Physiol.*, 1912, 5, 347—372).—Potassium salts give rise to two types of contraction in cardiac muscle (frog), which are termed "tonic contraction" and "contraction effect." Some salts produce one, others the other effect, but all temporarily abolish rhythmical activity, and may produce "heart block" if perfused at high pressure. The effects are mainly explained by considering that these salts displace calcium salts, and the various calcium salts are displaced at varying rates. Seasonal variations noted are explained as due to changes in the balance between calcium and potassium salts in the heart muscle; temperature may also be a factor.   W. D. H.

Physiology and Pharmacology of the Cardiac Vagus. I. The Influence of Chloral Hydrate on the Result of Vagus Stimulation. OTTO LOEWI (*Arch. expt. Path. Pharm.*, 1912, 70, 323—342).—Intravenous injection of chloral hydrate in small doses has no effect on blood pressure and heart rate, but almost completely annuls the return of the heart-beat during vagus stimulation. Large doses abolish vagus excitability. Camphor has also no effect on blood-pressure or pulse rate, but influences vagus stimulation in a similar way. The action of pilocarpine and muscarine is similarly weakened.   W. D. H.

Physiology and Pathology of the Cardiac Vagus. II. The Importance of Calcium for Vagus Action. OTTO LOEWI (*Arch. expt. Path. Pharm.*, 1912, 70, 343—350).—Partial removal of calcium by small amounts of oxalate increases the excitability towards electrical stimuli of various nerves; the least affected is the pelvic nerve, but the chorda tympani and especially the vagus are profoundly affected. This is not inhibited by calcium. The action of muscarine on the frog's heart occurs after it is rendered poor in calcium,

or free from calcium. The paralysis of the vagus by pilocarpine or muscarine in mammals and frogs is not influenced by calcium.

W. D. H.

Physiology and Pharmacology of the Cardiac Vagus. III. Vagus Excitability and Vagus Poisons. OTTO LOEWI (*Arch. expt. Path. Pharm.*, 1912, **70**, 351—368).—In very small doses muscarine (and pilocarpine) increases vagus excitability in the frog. In vagus paralysis produced by these drugs there exists neither in frog nor rabbit any automatic ventricular action. The effect of prolonged electrical stimulation of the nerve is either increased by muscarine or unaffected by it, according to the duration of the stimulation or the dose of the poison. Similarly, the pilocarpine effect can be superposed on the muscarine effect, or vice versa. Physostigmine does not sensibilise the muscarine or pilocarpine action. The action of pilocarpine and muscarine is considered to be on the myoneural junction.

W. D. H.

The Behaviour of Acetic Acid in the Artificial Perfusion of the Liver. ADAM LOEB (*Biochem. Zeitsch.*, 1912, **47**, 118—126). —Various results obtained by Embden and his school are recapitulated, and reasons are given as to why acetic acid might be expected as a normal degradation product of fats, carbohydrates, and proteins, especially through the intermediation of pyruvic acid. As no evidence could be obtained of the formation of acetic acid when pyruvic acid was added to blood in a perfusion experiment, the effect of adding the former acid itself to the blood was investigated. It was found that, during perfusion, a very marked disappearance of this acid took place. It was also found, without exception in ten experiments, that the addition of acetic acid to the perfusion of blood caused a marked increase in the formation of acetoacetic acid. The mechanism of this reaction is discussed, and it is provisionally suggested that the degradation of acetoacetic into acetic acid is a reversible process :

$$CH_3 \cdot CO \cdot CH_2 \cdot CO_2H \rightleftharpoons 2CH_3 \cdot CO_2H,$$
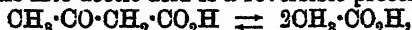
and for this reason the acetic acid may inhibit the degradation of the acetoacetic acid normally formed to simpler products.

S. B. S.

The Fate of Glyoxylic Acid in the Animal Body. GEORG HAAS (*Biochem. Zeitsch.*, 1912, **46**, 296—306).—On incubation of minced liver of various animals with glyoxylic acid, this substance partly disappeared, but no definite degradation products were isolated. Its perfusion through rabbit's liver gave rise to formic acid, and this acid could also be isolated in the urine of a dog which had received glyoxylic acid *per os*.

S. B. S.

The Destruction of Alkaloids by the Body Tissues. A. J. CLARK (*Quart. J. expt. Physiol.*, 1912, **5**, 385—398).—The liver of frog and rabbit possesses the power of destroying atropine ; this persists after the cells are destroyed, and is due to a soluble substance resembling an enzyme in its action. The heart and kidneys of the frog and the

blood of the rabbit have the same power in a less degree, but all the other tissues are destitute of the power. None of the tissues in cat, rat, and dog has the power, and the minimal lethal dose of atropine is highest in those animals the livers of which can destroy it.

W. D. H.

The Distribution of Nitrogen in Autolysis, with Special Reference to Deaminisations. GERTRUDE D. BOSTOCK (*Bio-Chem. J.*, 1912, 6, 388—415).—The following nitrogen fractions in the autolysis products of liver were determined: ammonia, amide nitrogen, and amino-acid nitrogen. It was necessary to ascertain these factors in order to determine the fate of ammonium salts and amino-acids when digested with liver tissue. In fresh liver the soluble nitrogen fraction is characterised by its low ammonia and amino-nitrogen content. The latter, however, increases after forty-eight hours' incubation at the expense of the undetermined nitrogen fraction. The rate of autolysis reaches its maximum within this period. Acids stimulate and alkalis depress the autolysis rate, and the distribution of nitrogen differs under these two conditions. Acids cause a lower and alkalis a higher percentage of ammonia and undetermined nitrogen fractions than in the control autolyses without addition of either acid or alkali. The reverse is the case with regard to the amide or amino-acid nitrogen. Putrefactive organisms cause a higher percentage of ammonia and undetermined nitrogen. No evidence could be obtained of the formation of amide nitrogen from ammonium sulphate or lactate when digested with liver pulp. There is also no evidence of liberation of ammonia from glycine. In view of the formation of ammonia by putrefactive organisms, any statements as to the liberation of this substance from amino-acids when digested with tissues must be received with caution.

S. B. S.

The Permeability of the Kidneys to Sugar after Repeated Injections of Adrenaline. ARTUR VON KONSCHEGG (*Arch. expt. Path. Pharm.*, 1912, 70, 311—322).—Diuresis which follows the injection of adrenaline is independent of glycosuria. After salt diuresis is produced, it is not possible to produce glycosuria by such injections; the blood contains no excess of sugar, but the kidneys themselves contain more than normal. Inhibition of glycosuria is not brought about by the kidneys being unable to take up sugar from the blood.

W. D. H.

The Amount of Silicic Acid in Human Thyroid Glands. HUGO SCHULZ (*Biochem. Zeitsch.*, 1912, 46, 376—392).—The mean content of the normal glands from the neighbourhood of Greifswald was 0·0084%, and that of pathological glands from the same district, 0·0175%. The pathological glands from Zurich, on the other hand, contained as much as 0·0434%. The author, nevertheless, gives reasons for not believing that goitre is due to water containing silicic acid, and he failed to produce the disease experimentally in animals which had received over long periods water containing relatively large quantities of the acid.

S. B. S.

The Creatine-splitting Enzyme of the Parathyroids and the Suprarenals. ALBERT HOLMES ROWE (*Amer. J. Physiol.*, 1912, 31, 169).—A creatine-splitting enzyme is present in the thyro-parathyroid tissue ; this confirms the results of Gottlieb and Stau-gassinger. A similar enzyme is found in suprarenal extract. There is no evidence that either the parathyroids or the suprarenals contain a creatine-splitting enzyme which can be activated by the other.

W. D. H.

The Chemistry of Normal and Eclamptic Placenta. L. MOHR and W. HEIMANN (*Biochem. Zeitsch.*, 1912, 46, 367—373).—Estima-tions were made of the water content, total phosphoric acid and nitrogen, ether soluble substances, cholesterol, neutral fat, and diastearyllecithin. The last-named was appreciably larger in normal placenta than in cases of eclampsia. There was no marked difference in the other factors.

S. B. S.

The Physico-chemical Basis of a Theory of Muscular Contraction (Zuntz's Theory). WILLIAM N. BERG (*Pflüger's Archiv.* 1912, 149, 195—220. Compare A., 1912, ii, 1077).—A critical and antagonistic discussion of Zuntz's theory ; the main point is that lymph contains practically no carbon dioxide in the simple gaseous condition, and that when gases are dissolved in water they behave differently from substances in true solution, and, with the exception of hydrogen chloride and ammonia, exert no osmotic pressure. The carbon dioxide which is formed by muscular activity has therefore no osmotic pressure.

W. D. H.

The Anaphylactic Reaction of Plain Muscle in the Guinea Pig. HENRY H. DALE (*Proc. physiol. Soc.*, 1912, xxvii—xxix ; *J. Physiol.*, 45).—Experiments on the plain muscle (uterus) of the guinea pig sensitised to horse-serum and other proteins ; it reacts in response to minute doses (one in a million) of the specific antigen ; after response it is completely desensitised ; it can be re-sensitised by soaking in the serum of sensitised guinea pigs. The time relations of the reaction exclude the production of a poison by parenteral digestion. The antigen acts on the sensitised muscle like a stimulant drug, the peculiar feature being that the "receptive or anti-substance" is de-tachable. There is much evidence in favour of the view that the anaphylactic anti-substance is identical with precipitin.   W. D. H.

Synthesis of Lecithin in the Hen and the Character of the Lecithins Produced. ELMER V. McCOLLUM, J. G. HALPIN, and A. H. DRESCHER (*J. Biol. Chem.*, 1912, 13, 219—224. Compare A., 1912, ii, 368).—Further experiments are given to show that hens fed on a diet free from lipoids produce eggs which contain lecithin or lecithins. These differ in the nature of their fatty acid radicles, and variation may be produced by the nature of the lipoids of the diet.

W. D. H.

Red Colouring Matter of Boiled Crabs. EUGÈNE GRANDMOUGIN (*Chem. Zeit.*, 1912, 36, 1377—1378).—The change of colour observed

when crab-shells are boiled has been attributed by Kornfeld to the formation of alizarin-red, which depends on the presence of alizarin and aluminium oxide in the unboiled shell.

The author points out that the presence of anthraquinone in the normal organism has not previously been observed. He also finds that the colouring-matter of crab- and lobster-shell, unlike alizarin-red, is soluble in alcohol or ether, and is very sensitive to light. When dissolved in alcohol, it shows characteristic absorption bands in the green portion of the spectrum which differ completely from the bands given by alizarin. It possesses no dyeing power. Finally, the presence of compounds of aluminium in the shell could not be detected with certainty.

The exact nature of the colouring matter has not been determined, but the presence of anthraquinone derivatives is extremely improbable.
                                                                    H. W.

The Bio chemistry of Termites. The Chemical Composition of the Fæcal Stalactites of Entermes monoceros. KONRAD SCHUBEL (*Arch. expt. Path. Pharm.*, 1912, 70, 303—310).—The tree ant of Ceylon protects its nest by so-called stalactites, and it has been surmised that these contain cantharidin or some similar poison. The present work shows that the material consists of an organic non-toxic substance with a small amount of inorganic salts. The ash has the following percentage composition: SiO_2, $45\cdot2$; P_2O_5, $1\cdot09$; $Fe_2O_3 + Al_2O_3$, $23\cdot5$; Mn_3O_4, $1\cdot05$; CaO, $14\cdot25$; MgO, $1\cdot5$, and $K_2O + Na_2O$, $13\cdot3$. By distillation in a vacuum it was proved that the fæcal matter contains preformed an olefine, probably $C_{35}H_{70}$, m. p. $75°$. These animals live almost exclusively on flies and algæ.   W. D. H.

Metabolism Studies on the Cold-blooded Animals. I. The Urine of the Fish. W. DENIS (*J. Biol. Chem.*, 1912, 13, 225—232). —The urine of the dog-fish is clear, odourless, and almost colourless; it is acid to litmus. It darkens and becomes cloudy when kept. It gives the murexide reaction, and contains creatinine, but not creatine. The following is the average composition, expressed in grams per litre: total nitrogen, $4\cdot2$; urea nitrogen, $3\cdot4$; ammonia nitrogen, $0\cdot3$; chlorides (as $NaCl$), $12\cdot8$; phosphates (as P_2O_5), $4\cdot5$; total sulphur (as SO_3), $7\cdot1$, and total sulphates (as SO_3), $3\cdot4$. The goose fish (*Lophius piscatorius*) is the only teleost so far investigated; in general appearance and reaction, the urine resembles that of the dog-fish; uric acid, creatine, and creatinine were absent. The one specimen examined contained, in milligrams per litre, total nitrogen, 400; urea nitrogen, 248, and ammonia nitrogen, 2.   W. D. H.

Behaviour of Alicyclic Compounds in Coupling with Glycuronic Acid in the Organism. JUHO HAMÄLÄINEN (*Chem. Zentr.*, 1912, ii, 854—856; from *Skand. Arch. Physiol.*, 1912, 27, 141—226). —A number of terpenes and allied compounds dissolved in olive oil were fed to rabbits. The urine produced was collected, and the coupled glycuronic acids formed were either isolated or the products of their hydrolysis by acids were examined.

Menthene in this way gave rise to a product which on hydrolysis yielded a *hydrocarbon*, $C_{10}H_{16}$, b. p. 178—180°, that on hydration gave a dihydric *alcohol*, $C_{10}H_{20}O_2$, m. p. 55—59°, which may be *p*-menthan-2 : 4-diol. Dihydrocarveol in the same way yielded a menthadiene, $C_{10}H_{16}$, b. p. 179—181°, which on oxidation gave dihydrocarvone, and on hydration furnished *p*-menthan-2 : 8-diol. Terpin yielded a menthadiene, b. p. 178—181°, which gave terpin hydrate and terpineol on hydration, and terpenylic acid on oxidation with chromic acid. Menthone, before coupling with glycuronic acid, appears to be oxidised to Δ^4-menthen-3-one, since the latter is produced on hydrolysis of the coupled product.

Thujone is apparently first converted in the organism into *p*-menthan-2-one-4-ol by addition of 1 mol. of water. On hydrolysis the coupled product yields carvenone, whilst oxidation with sodium hypobromite gives ω-dimethyllævulic acid. Thujyl alcohol, under like conditions, seems to be converted into *p*-menthan-2 : 4-diol, since the latter is formed on hydrolysis of the coupled glycuronic acid produced in the organism.

Sabinol yields *sabinolglycuronic acid*, $C_{16}H_{24}O_7$, m. p. 82—83°, as a colourless, glassy mass, giving crystalline *sodium* and *strychnine* salts. The latter has m. p. 196—197°, $[\alpha]_D^{20}$ – 39·66° in alcohol, and crystallises with $2H_2O$ in needles from hot water. Sabinene yields a coupled product, which on hydrolysis with 5% sulphuric acid gives a gelatinous substance that on hydrolysis with stronger acid yields Δ^1-menthenone (?).

Pinene and nopinene appear to undergo oxidation before coupling, since the coupled product yields *p* cymene on hydrolysis. Camphane is also oxidised in the organism, and yields a mixture of d- and l-*bornolglycuronic acids*, $C_{16}H_{26}O_7$, m. p. 163—165°, $[\alpha]_D^{20}$ – 56·91°, as a colourless, crystalline mass.

l-Fenchyl alcohol furnishes *fenchylglycuronic acid*, $C_{16}H_{26}O_7,H_2O$, m. p. 124—126°, $[\alpha]_D^{21}$ – 63·07°, crystallising from acetone and yielding well crystallised salts. 1-iso-*Fenchylglycuronic acid*, m. p. 140—150°, $[\alpha]_D^{20}$ – 81·02°, is amorphous.

Camphenilolglycuronic acid, $C_{15}H_{24}O_7$, m. p. 150—153°, is a colourless mass, obtained by the use of either camphenilol or camphenilone, the latter apparently undergoing initial reduction in the organism.

α-Santenol gives rise to *α-santenolglycuronic acid*, $C_{15}H_{24}O_7,H_2O$, m. p. 160—161°, $[\alpha]_D^{11}$ – 56·6°, a colourless mass, which yields crystalline salts. *β-Santenol* also couples unchanged, furnishing β-santenolglycuronic acid, which was not isolated, but was found to yield santene on acid hydrolysis. Santenone is first oxidised to *santenonol*, $C_9H_{14}O_2$, m. p. 92—93°, crystallising in colourless leaflets, giving a crystalline *semicarbazone*, m. p. 222—223°, and yielding santenic acid on oxidation. *Santenonolglycuronic acid*, $C_{15}H_{22}O_8$, yields a crystalline *strychnine* salt, $C_{36}H_{44}O_{10}N_2,2H_2O$, m. p. 171—172°, and gives santenonol on hydrolysis.

Camphene hydrate couples unchanged with glycuronic acid in the organism, and the product on hydrolysis gives camphene, by loss of water from the regenerated camphene hydrate. T. A. H.

The Relationships between Tumour Cells and Blood-serum. ERNST FREUND and GISA KAMINER (*Biochem Zeitsch.*, 1912, 46, 470—482).—The property possessed by normal sera of destroying carcinoma cells is due to an ether-soluble, nitrogen-free fatty acid. The property of carcinomatous serum of protecting carcinomatous cells from destruction, and of giving specific turbidity with saline extracts of carcinomas, is due to the euglobulin (nucleoglobulin) fraction of the serum which is soluble in sodium carbonate, and is distinguished from normal nucleoglobulin by its high content of carbohydrate group. The property of carcinoma extracts of giving turbidities with carcinomatous sera is due to a nitrogen-free carbohydrate compound. The specific precipitates of carcinomatous and sarcomatous extracts with their respective sera are characterised in the former case by carbohydrate-rich substances, and in the latter case by groups yielding the biuret reaction. The carcinomatous precipitates carry down from solution added carbohydrates, whereas the sarcomatous precipitates carry down added peptone. The tumour cells themselves show a similar adsorptive capacity, the carcinomatous cells binding sugar, lecithin or nuclein, whereas the sarcomatous cells bind peptones and nuclein. S. B. S.

The Interstitial Granules (Liposomes) in Fatty Metamorphosis of Striated Muscle. E. T. BELL (*J. Path. Bact.*, 1912, 17, 147—159).—Fatty metamorphosis may be produced in the leg muscles of a rat by applying a ligature round the thigh ; in the fibres of these muscles the liposomes stain with greater intensity, and are much larger than normal ; this is especially the case in well nourished animals, or if the rat is fed on fat. Pathological fatty metamorphosis is an exaggeration of a normal process, and consists in an increase in the size, staining capacity, and often the number of liposomes. Part of the fat is already present when the process begins. The increase of size is probably due to the accumulation of triolein. W. D. H.

Nature of the So-called Klausner Serum Reaction. G. KLAUSNER (*Biochem. Zeitsch.*, 1912, 47, 36—58).—The author has already shown that sera from certain cases of syphilis yield a precipitate when diluted with three times the volume of water. This property is lost if the serum is previously extracted with ether, and is restored by the addition to the serum of the lecithin–cuorin–cephalin fraction of brain lipoids. A serum can also be rendered non-precipitable by water if heated, but in this case the precipitability (activation) is not restored by lipoids. A serum activated by brain lipoids can also be inactivated by heating. The property of restoring activity by lipoids is not destroyed by heating. An artificially activated serum (by lipoids) if inactivated by heat is not rendered active again by the addition of fresh serum ; hence, the activating property of lipoids is best if they are heated in the presence of serum. In all cases both of artificial and natural precipitin reactions, the optimal condition for precipitation is dilution with three times the volume of water. The natural precipitin reaction, when destroyed by heat, is not restored on the addition of fresh serum. A positive serum, inactivated by extraction with ether, can be reactivated

by the addition of the ethereal extract, which can also activate a normal inactive serum. Strong concentrations of the ethereal extracts of normal serum, dissolved in water, can also activate a normal serum. These results indicate that the precipitation is not due to globulins, and that in syphilitic sera the abnormalities are due to excess of lipoids.   S. B. S.

Bence-Jones Proteinuria. E. PROVAN CATHCART and J. HENDERSON (*J. Path. Bact.*, 1912, **17**, 238—248).—A detailed account of the examination of the urine in a case of this disease. The general result of an examination of the protein present is that the findings of Hopkins and Savory (A., 1911, ii, 417) are confirmed.   W. D. H.

The Action of Carbon Dioxide on the Vascular System. S. ITAMI (*J. Physiol.*, 1912, **45**, 338—344).—Small percentages of carbon dioxide produce a rise of arterial pressure mainly by increasing the force of the heart. Higher percentages (over 8%) produce increased constriction of the arterioles by stimulating the vaso-motor centre, and probably from an increased activity of the suprarenal glands.   W. D. H.

Diuretic Action of Mercury Preparations. D. FERRON (*Chem. Zentr.*, 1912, ii, 370; from *Arch. Farm. sperim.*, 1912, **13**, 283—288). —Intravenous injection of doses of 0·000010 to 0·000025 gram-equivalents of mercuric chloride per kilo. of body-weight causes in rabbits an appreciable diuresis, but in larger doses the effect is less than that of the saline injection alone, owing to the toxic properties. A simultaneous injection of sodium chloride decreases the toxic effects, and, vice versa, mercuric chloride diminishes the toxic effects of hypertonic sodium chloride solution.   S. B. S.

Action of Mercury Preparations on Spirochaete Diseases. I. Chemical-therapeutic Action of Mercury Compounds, Especially of a New Mercury Preparation which Strongly Attacks Spirochaete, but is only very Slightly Poisonous WILHELM KOLLE, M. ROTHERMUND, and S. PESCHIÉ (*Chem. Zentr.*, 1912, ii, 1574—1575; from *Deut. med. Woch.*, 1912, **38**, 1582—1585).—The therapeutic action of many mercury preparations, such as colloidal mercury, mercury peptonate, dinitromercuridibenzoic acid, sulphaminophenyldimethylpyrazolonemercury, etc., has been examined. The aliphatic compounds do not differ very much in their action, but the benzene and pyrazolone compounds show many differences in toxicity and in the relation of the curative to the toxic dose. Sulphamino-compounds show a great lowering of the poisonous nature of mercury preparations without a diminution in their spirillocidal properties, and sulphaminophenyldimethylpyrazolonemercury is especially to be recommended.   J. C. W.

Action of Mercury Preparations on Spirochaete Diseases. II. The Toxicology and Pharmacology of Some Mercury Compounds. J. ABELIN (*Chem. Zentr.*, 1912, ii, 1575; from *Deut. med. Woch.*, 1912, **38**, 1822—1825. Compare preceding abstract).—The poisonous nature of mercury compounds is influenced by their

chemical constitution ; the introduction of sulpho- or amino-groups or of doubly-linked carbon atoms diminishes their toxicity. The most poisonous compounds are those in which the mercury is easily ionised, such as mercuric chloride. After injection of mercury preparations, the metal is always found in the liver.   J. C. W.

The Sugar of the Blood and Urine under the Influence of Continuous Adrenaline Infusion. M. J. GRAMENITZKI (*Biochem. Zeitsch.*, 1912, 46, 186—209).—Adrenaline was continuously administered to rabbits by Straub's infusion apparatus, and the effect on the sugar content in the blood and urine with varying dilutions of the drug was ascertained. It was found that there is in general a proportionality between the strength of the adrenaline stimulus, and both the resulting hyperglycæmia and glycosuria. Under urethane narcosis, the amount of adrenaline necessary to produce glycosuria is below the normal. Under these conditions, the strength of the adrenaline stimulus necessary to produce glycosuria is less than that required to raise the blood-pressure. The adrenaline administration increases the diuresis within a few minutes, and this effect is often, but not always, accompanied by glycosuria. The diuretic effect of urethane is to be ascribed to its urea components, whereas its glycosuric effects can only be partly ascribed to these.

Under urethane narcosis, artificially introduced sugar disappears more slowly than in normal animals ; it also disappears more slowly from bound animals than from animals which are free. Venesection causes a distinct but slight hyperglycæmia, which is sometimes accompanied by glycosuria. The effects of the narcotic, etc., were investigated in some detail in view of criticisms on Ritzmann's work, which was also carried out in Straub's laboratory. In experiments on non-narcotised animals, it was found that the proportionality between the adrenaline stimulus and the effects was more marked than in the narcotised animals. The primary effect is hyperglycæmia, which can be quite marked (up to 0·2%) even when there is no glycosuria. The smallest stimulus necessary to produce glycosuria is higher in non-narcotised than in narcotised animals. The diuretic action of adrenaline follows definite laws, and is independent of the glycosuric effect. The general theory of the drug action is discussed.   S. B. S.

Effect of Adrenaline on the Pulmonary Circulation. E. M. TRIBE (*Proc. physiol. Soc.*, 1912, xx—xxii ; *J. Physiol.*, 45).—The conflicting results of previous workers on this question are probably due to the use of different preparations. Adrenaline preparations free from preservative cause constrictions at body temperatures. Preparations of adrenaline chloride preserved with 0·5% chloretone cause distinct dilatation of the pulmonary vessels. The constriction obtained with pure adrenaline is, however, hardly comparable with that seen in organs supplied by vaso-motor nerves, and the question of the existence of such nerves in the lung-vessels is left undecided.

                                                         W. D. H.

The Vascularity of the Liver. VIII. The Influence of Adrenaline on the Arterial Inflow. RUSSELL BURTON-OPITZ (*Quart. J. expt. Physiol.*, 1912, 5, 309—324).—The complex nature of the blood supply of the liver renders the interpretation of records a matter of difficulty, and much of this and the following papers is devoted to a discussion of this question. There appears, however, no doubt that adrenaline constricts the arterioles of the liver, and leads then to a rise of pressure in the hepatic artery and an increase in the arterial inflow, the general blood-pressure being also raised. This is followed by a period of lessened inflow, although the hepatic pressure is still high, but the general pressure is only slightly elevated. Exceptions to this rule are explained by the fact that an injection of adrenaline does not necessarily imply that it enters the hepatic artery; it might be swept past the orifice of the artery; a similar accident in the case of arteries supplying other organs might explain unexpected results there.   W. D. H.

The Vascularity of the Liver. IX. Influence of Amyl Nitrite on the Arterial Inflow. RUSSELL BURTON-OPITZ (*Quart. J. expt. Physiol.*, 1912, 5, 325—328).—Inhalation of amyl nitrite causes a fall of general arterial pressure, but also causes a local change in the liver circulation. The fall of pressure in the hepatic artery is proportional to the general fall. On discontinuing the inhalation the pressure returns very slowly to normal. The arterial inflow is directly proportional to the systemic pressure, and the local changes are attributed wholly to the general effect.   W. D. H.

The Vascularity of the Liver. X. The Influence of Adrenaline on the Venous Inflow. RUSSELL BURTON-OPITZ (*Quart. J. expt. Physiol.*, 1912, 5, 329—342).—Evidence is adduced that the liver possesses two separate motor mechanisms, one in the terminals of the hepatic artery, and the other in the radicles of the portal vein, both of which are stimulated by adrenaline.   W. D. H.

Metabolism Experiments in the Administration of Atophan. WITOLD SKORCZEWSKI and J. SOHN (*Chem. Zentr.*, 1912, ii, 1381; from *Zeitsch. expt. Path. Ther.*, 1912, 11, 254—263).—Experiments on normal persons and on sufferers from gout show that the administration of atophan causes an increase in the output of uric acid, which, however, falls off with subsequent doses, more purine bases being discharged. An alteration in the functions of the kidneys is presumed, for a retention of chlorides immediately follows the administration. The atophan urine always gives the diazo-reaction, which becomes weaker after several doses; it also gives the phenol reaction with bromine water, a dirty rose-coloured precipitate with Millon's reagent, a yellow precipitate with phosphotungstic acid, and a green colour with a mixture of ammonium sulphate and ammonia.

                                                        J. C. W.

Why Does Atophan Increase the Excretion of Uric Acid? WITOLD SKÓRCZEWSKI (*Chem. Zentr.*, 1912, ii, 1679; from *Zeitsch. expt. Path. Ther.*, 1912, 11, 501—507. Compare preceding abstract),—

The action of atophan is presumed to be an oxidation disturbance, of which the interference in the degradation of uric acid is a special case. This affords an explanation of the variations in uric acid values, the increase in neutral sulphur, and the appearance of the diazo-reaction in atophan urine. J. C. W.

The Formation of Phenol from *p*-Cresol in the Organism of the Dog. MAX SIEGFRIED and R. ZIMMERMANN (*Biochem. Zeitsch.*, 1912, 46, 210—224).—In view of Baumann's conceptions as to the degradation of tyrosine in the organism through *p*-cresol and *p*-hydroxy-benzoic acid to phenol, the effect of the administration of *p*-cresol was investigated, and it was found to yield phenol; 32—48% of the phenolic substances administered were recovered in the urine, of which 23—46% was in the form of phenol. Various modifications in the technique of phenol and cresol estimation are given, chiefly with regard to the method of bromination, and the addition of sufficient alkali before evaporating the urine to prevent loss of phenol.

S. B. S.

Formation of Glycine in the Body. II. ALBERT A. EPSTEIN and SAMUEL BOOKMAN (*J. Biol. Chem.*, 1912, 13, 117—132).—Free leucine does not yield glycine, although it undergoes decomposition in the body. When benzoyl-leucine is given with benzoic acid, the output of hippuric acid is much greater than the leucine alone allows. Phosphorus poisoning causes no increased production of glycine or hippuric acid. Phosphorus plus benzoic acid has also no such effect unless the animal is fasting; then the increase must be due to massive disintegration of protein. Much of the glycine liberated on feeding with benzoic acid must be the result of a synthesis in the body. W. D. H.

Tolerance to Nicotine. WALTER E. DIXON and W. E. LEE (*Quart. J. expt. Physiol.*, 1912, 5, 373—382).—A person tolerant to nicotine may be so because nicotine is not absorbed, but this is unlikely. A second explanation may be that it is more readily destroyed by the tissues. The present experiments were made on rabbits, and in thirteen out of sixteen experiments, tolerance was established, the drug being injected under the skin, or into the blood-stream. The analyses of the tissues show that the second explanation given above is correct, but that all the cells of the body do not possess the power of destroying nicotine in equal measure: the liver is the most effective. Evidence is adduced that the destruction is probably oxidative and due to the action of an enzyme. W. D. H.

The Oxidation of *p*-Phenylenediamine by Animal Tissues. FR. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1912, 46, 317—342).—It is shown in investigations of the oxidative functions of tissues that the *p*-phenylenediamine reaction is better than the indophenol reaction. All tissues can oxidise this substance. The amount of oxygen consumed was in most cases measured, and it was found that in the accessory respiration of the tissues the amount consumed

was the sum of that used up by the tissues, when without the reagent plus the amount necessary to oxidise the reagent. In the primary respiration, on the other hand, the p-phenylenediamine oxidation partly replaced the tissue respiration. The oxidation is most intensive in the heart, red muscles, liver and kidney, and much less in the pancreas, spleen, and lungs. With the exception of the pancreas, the tissues maintain their oxidative capacity for a long time after death. Under similar conditions of experiment, most tissues use up the same amount of oxygen for oxidising p-phenylenediamine as they do for succinic acid; the brain, however, uses up more. In muscles and liver, no more oxygen is used up if both substances are present than if they are present alone. The blood is an energetic oxidiser, but not the serum, and the action appears to be due mostly to the hæmoglobin, as in the blood of some animals, the oxidative capacity remains after heating to 60°, or treatment with pancreatin. This is not even lost after heating the blood with mineral acids. An aqueous extract of liver inhibits the oxidative capacity of the blood, and the inhibitory action is not destroyed by warming to 60°. Blood has no appreciable oxidative action on succinic acid.   S. B. S.

The Influence of Various Factors on the Oxidation of p-Phenylenediamine by Animal Tissues. FR. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1912, 46, 343—366).—Small amounts of acid or alkali inhibit oxidation. There is no marked optimal temperature of reaction between 30° and 50°, but the action is lost by heating tissues to 60° for ten minutes. In medium concentrations, salts accelerate the reaction, exerting an inhibitory action at higher concentrations. Up to a certain limit the rate of oxidation increases with an increase of the concentration of the p-phenylenediamine. The oxydase is not washed out from the tissues by water, and the washed tissues still contain the oxydase. In oxygen, the reaction is more energetic than in air. The oxydase is destroyed by treating the tissues with alcohol or acetone, or with weak solutions of mineral acids. Aqueous extracts of tissues oxidise in presence of hydrogen peroxide, and this function is not lost on heating. The washed residue of muscular tissue will not oxidise in the presence of the peroxide after heating to 60°. Treatment of tissue with pancreatin diminishes the oxidative capacity. Both fresh and heated pancreatin increase the oxidative capacity of the vegetable polyphenoloxydases. Catalysts accelerating the oxidation of p-phenylenediamine and succinic acid are distinguishable from other oxydases by the facts that they are not dissolved out by water, and are destroyed by alcohol, acetone, or trypsin. With the exception of those of the brain, the catalysts appear to be identical.   S. B. S.

Pharmacology of Picrotoxin, Picrotin, and Picrotoxinin. ALFREDO CHISTONI (*Chem. Zentr.*, 1912, ii, 371—372; from *Arch. Farmacol. sperim.*, 1912, 13, 220—240).—Picrotoxin and picrotoxinin, in concentration 1 in 2000, reduce the tone and the amplitude of the contractions of smooth muscle, but in concentration 1 in 10,000 they increase the amplitude and diminish the number of contractions,

and either do not influence or slightly increase the tone of smooth muscle ; picrotin is inactive.

All three substances, in a concentration of 1 in 2000, slightly increase the tone of striped muscle.

The frequency and contraction of the amphibian heart are affected by picrotoxin and picrotoxinin, due to their action on the muscle ; picrotin is inactive.

Picrotoxin and picrotoxinin intravenously injected in dogs reduce the pulse and increase the blood pressure, due to stimulation of the pneumogastric and the vasomotor centres.

All three substances (1 in 2000—4000) still the isolated hearts of cats and rabbits, but this effect ceases when the poisons are removed. In a concentration of 1 in 80,000, picrotoxin at first quickens and then slows the heart's action, and these effects are not inhibited by the previous application of atropine. Picrotoxinin (1 in 80,000) at first strengthens and quickens the heart's action by its effect on the vagus, but finally stills the heart by direct action on the muscle fibres. Picrotin (1 in 40,000) accelerates the heart-beats and reduces the strength of the pulse. T. A. H.

The Poisonous Nature of Methyl and Ethyl Alcohols. ALEXANDER LANGGAARD (*Chem. Zentr.*, 1912, ii, 1382—1383; from *Berl. klin. Woch.*, 1912, 49, 1704).—Methyl alcohol is more poisonous than ethyl alcohol when taken in repeated small quantities, but ethyl alcohol is much more dangerous when taken in a single large dose. J. O. W.

Hæmolytic Substances obtained from Serum, and the Vitellus of Egg, Submitted to the Action of Venoms. C. DELEZENNE and (Mlle.) S. LEDEBT (*Compt. rend.*, 1912, 155, 1101—1103. Compare *ibid.*, 1911, 152, 790; 153, 81).—Cobra venom acts on the serum of horse blood or the vitellus of egg, giving rise, by diastatic action of the venom on the lecithin, to *hæmolysin*, which differs from lecithin in that it is soluble in water and insoluble in ether, and its molecule does not contain any unsaturated fatty acids (oleic acids). It resembles lecithin in its solubility in alcohol.

In the case of the serum the venom-serum mixture attains a maximum hæmolytic power, which then decreases until the mixture is inactive. At the same time a very fine precipitate of calcium soaps (palmitate and stearate) is produced. This diminution in activity, which is peculiar to serum, corresponds with further decomposition of the hæmolysin, and if the serum is dialysed prior to addition of the venom, the second stage in the action does not occur, and it behaves in the same manner as the vitellus of egg. The liquid resulting from the dialysis of the serum produces this secondary effect on addition to a venom-vitellus mixture. W. G.

Chemistry of Vegetable Physiology and Agriculture.

A Hygienic Pipette for Bacteriological and Chemical Work. SERGEI TSCHACHOTIN (*Centr. Bakt. Par.*, 1912, i, 67, 319—320) —The pipette is intended to facilitate the removal of liquid cultures of pathogenic organisms, volatile poisonous compounds, or liquids above flocculent precipitates. A double-bored rubber cork is cut transversely, and between the two parts an ordinary rubber cap, such as is used for closing bacterial tube-cultures, is interposed and the three cemented together. Holes are made through the rubber cap with a hot needle, and two tubes are introduced: (*a*) a short straight one projecting slightly above and below the cork; (*b*) a siphon tube having the longer arm through the cork. A test-tube, having a diameter slightly larger than that of the rubber cork, is used as receiver, and closed by means of the flange of the rubber cap. The short arm may then be placed in the liquid to be pipetted off, and the cork of the pipette depressed slightly into the tube; the short glass tube is then closed by the fore-finger and the cork raised slightly. By this means a sufficient vacuum is created in the tube to cause the liquid to siphon over, and the flow is stopped by raising the short arm out of the liquid.
                                                            H. B. H.

Detection of Chitin in Bacteria. A. VIEHOEVER (*Ber. Deut. botan. Ges.*, 1912, 30, 443—452).—Chitin was found to be present in a number of bacteria, and the occurrence of glucosamine in bacterial material is attributed chiefly to the abundant presence of chitin rather than to glucoproteins.
The results are of interest in removing a supposed difference between fungi and bacteria. That fungi contains chitin has been known for a long time.   N. H. J. M.

Gas Metabolism of Bacteria. I. Fermentation of Dextrose by Bacillus coli, B. typhosus, and Bacterium welchii. FREDERICK G. KEYES and LOUIS J. GILLESPIE (*J. Biol. Chem.*, 1912, 13, 291—304). —The evolution of gas accompanying bacterial growth on media containing dextrose was studied by an exact method. Dextrose peptone media yield with *B. coli* more carbon dioxide than hydrogen on anaerobic fermentation; on a medium of ammonium lactate, di-sodium phosphate, and dextrose, nearly equal volumes of the two gases are obtained, the mean value of CO_2:H_2 being 1·06. This ratio is raised by the presence of oxygen, and by increase of phosphate. With *B. typhosus* the ratio is never below 19; with *Bacterium welchii* it is 1·48.   W. D. H.

Gas Metabolism of Bacteria. II. The Absorption of Oxygen by Growing Cultures of Bacillus coli and Bacterium welchii. FREDERICK G. KEYES and LOUIS J. GILLESPIE (*J. Biol. Chem.*, 1912, 13, 305—310).—For both micro-organisms the absorption of oxygen

simulates a unimolecular reaction, but the respiratory quotients are widely different. With varying oxygen pressures the ratio $CO_2 : H_2$, varies enormously for *B. coli*, but only slightly for *Bact. welchii.*

W. D. H.

Activation of Certain Processes of Microbic Oxidation by Uranium Salts. HENRI AGULHON and R. SAZERAC (*Compt. rend.*, 1912, **155**, 1186—1188).—A further study of the influence of uranyl acetate on *Mycoderma aceti* (compare A., 1912, ii, 973) and a comparative trial of the influence of uranyl nitrate and uranyl acetate on the sorbose bacteria. In the case of the acetic acid ferment, 1 part of uranyl acetate per 1000 gives an increase of 57% in the acid production, and even at a dilution of 1 in 100,000 an increase is shown at the end of seven days. With the sorbose bacteria, uranyl nitrate increases the rate of oxidation up to concentrations of 1 in 5000, but stops all fermentation at 1 in 1000. At all concentrations the acetate has a more favourable influence than the nitrate, and 1 part of the acetate in 10,000 produces an increase yield of 76%.

W. G.

Action of Infinitesimal Doses of Different Alkaline Substances, Fixed or Volatile, on the Vitality of Microbes. AUGUSTE TRILLAT and M. FOUASSIER (*Compt. rend.*, 1912, **155**, 1184—1186).—A study of the effect of adding minute quantities of various alkalis and organic bases to distilled water, to which is then added a drop of dilute, microbic, aqueous emulsion, containing no nutrient medium. The results, expressed in numbers of colonies formed, are given for the organism *M. prodigiosus*. With pure water there is slight growth for twenty-four hours and then the organism dies. Death is immediate with sodium hydroxide until a dilution of 1 in 50,000 is reached, and it is only in the case of ammonia, at dilutions of 1 in 50,000 and higher, that there is any marked increase in the number of colonies. With organic bases at higher orders of dilution (1 in 250,000) the number of colonies formed is greater with fatty amines than ammonia, and still greater with aromatic amines, although even here death ensues after fifteen days. The addition of traces of putrefactive gases to the distilled water allows cultivation to proceed even after three months.

W. G.

Putrefaction with Special Reference to the Proteus Group. LEO F. RETTGER and CLYDE R. NEWELL (*J. Biol. Chem.*, 1912, **13**, 341—346).—Putrefaction is taken to mean decomposition of protein with the production of malodorous substances. The power to bring this about has been attributed to various members of the *Proteus* group acting anaerobically. The present experiments do not confirm this.

W. D. H.

The Influence of Organic Acids on the Fermentation by Yeast. FRITZ JOHANESSOHN (*Biochem. Zeitsch.*, 1912, **47**, 97—117).— Formic acid and its higher homologues accelerate, in sufficiently dilute solutions, the rate of fermentation by yeast. The optimal action for each acid lies at the same molecular concentration. The smallest

quantities of the acids which stop fermentation do not kill the yeast. The stoppage of fermentation depends on the concentration of the acid and not on the absolute quantity present. The relationship between this concentration and the quantity of yeast is not a simple proportional one, but can be represented by the equation of a parabola. No appreciable adsorption of acids by yeast takes place. The essential action of acids is to be ascribed, not to the ions, but to the whole undissociated molecule.   S. B. S.

The Mechanism of Alcoholic Fermentation. ALEXANDER VON LEBEDEV (*Biochem. Zeitsch.*, 1912, 46, 483—489).—A reply to the criticisms of Harden and Young (A., 1912, ii, 670).   S. B. S.

The Mechanism of Alcoholic Fermentation. II. ALEXANDER VON LEBEDEV and N. GRIAZNOV (*Ber.*, 1912, 45, 3256—3272. Compare A., 1911, ii, 816, 1122).—Pure glyceraldehyde is fermented by extract of dried yeast directly to carbon dioxide and alcohol. Hexosephosphoric ester is not formed as intermediate compound as in the case of the fermentation of dihydroxyacetone.

It is further shown that during the fermentation of sugar by yeast extract, acetaldehyde is not reduced to alcohol; on the other hand, in the absence of sugar, yeast extract is able to reduce acetaldehyde to alcohol. This reduction is effected by an enzymatic process.

It is considered that during fermentation hexose is hydrolysed to two trioses, one of which, glyceraldehyde, loses hydrogen, forming pyruvic acid, which undergoes rearrangement immediately and breaks down into acetaldehyde and carbon dioxide (compare Neuberg, A., 1911, ii, 976, 1019, 1020). Methylglyoxal hydrate is possibly an intermediate product (Neuberg and Kerb, A., 1912, ii, 973); preliminary experiments indicate that methylglyoxal is fermentable by yeast juice.

The decomposition of hexose into two molecules of triose is regarded as a reversible reaction; it will proceed when part of the triose is withdrawn as hexosephosphate, so that this last compound acts as a regulating factor. The following complete scheme is suggested for fermentation :

$$4C_6H_{12}O_6 = 8C_3H_6O_3.$$

Glyceraldehyde.	Dihydroxyacetone.

$$4C_3H_6O_3 - 4H_2 = 4C_3H_4O_3$$
$$4C_3H_4O_3 = 4C_2H_4O + 4CO_2$$
$$4C_2H_4O + 4H_2 = 4C_2H_7 \cdot OH$$

$$4C_3H_6O_3 + 4RHPO_4 =$$
$$4C_3H_5O_3RPO_4 + 4H_2O$$
$$= 2C_6H_{10}O_4(RPO_4)_2 + 4H_2O$$
$$= 2C_6H_{12}O_6 + 4RHPO_4$$

$$2C_6H_{12}O_6 = 4C_3H_6O_3, \text{ etc.}$$
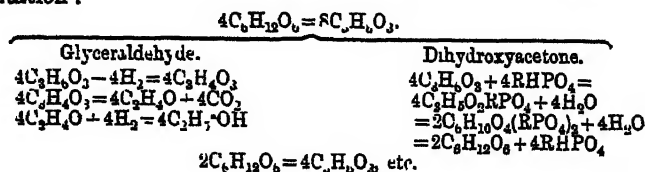
E. F. A.

Influence of Pressure on Alcoholic Fermentation. LÉON LINDET and L. AMMANN (*Bull. Soc. chim.*, 1912, [iv], 11, 953—956).—Regnard has shown already that under a pressure of 600 atmospheres yeast still ferments sugar solutions. In the present paper it is demonstrated that under such pressures as may occur in practice in fermenting liquids with yeast in closed vessels, the reproduction of

yeast and the fermentation go on at the same rate as under atmospheric pressure, although when the experiments are conducted under such conditions that the air is not renewed, fermentation and the multiplication of the yeast-cells take place more slowly, although the same production of carbon dioxide and alcohol is eventually reached.

T. A. H.

Is Ethyl Alcohol Produced by Yeast Fermentation in Absence of Sugar? CARL NEUBERG and JOHANNES KERB (*Chem. Zentr.*, 1912, ii, 1299—1300; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, 1, 114—120).—Since pyruvic acid is easily attacked by yeast with the formation of acetaldehyde (A., 1911, ii, 1019) it was expected that the ferment alone might be able to carry the reduction further. No alcohol could be found, however, but in the presence of sugar, much less aldehyde was formed than the amount of pyruvic acid destroyed would warrant. It seemed, therefore, that in normal alcoholic fermentation, a substance is produced which can reduce pyruvic acid or acetaldehyde to alcohol. Formic acid suggested itself, but was found to be without influence. Glycerol, however, had the effect of largely diminishing the output of acetaldehyde.   J. C. W.

The Primary Transformation of Hexoses by Alcoholic Fermentation. HANS VON EULER and TH. BERGGREN (*Chem. Zentr.*, 1912, ii, 1383—1384; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, 1, 203—218).—The addition of yeast extract to living yeast expedites fermentation by 100%, and the difference, ΔC, between the change in optical rotatory power and the carbon dioxide developed (compare A., 1912, ii, 377) is increased by 20%. Assuming that fermentation proceeds in two stages, hexose $\longrightarrow$ intermediate product and intermediate product $\longrightarrow$ alcohol and carbon dioxide, it follows that, if the extract contains only one co-enzyme the first stage will be accelerated, but if there is a co-enzyme in the extract appropriate to each stage, then the two reactions will be unequally accelerated according to the relative amounts of the co-enzymes. Sodium nucleate also increases the activity of living yeast.   J. C. W.

The Effect of Phosphates on the Work of the Proteolytic Enzymes in Yeast. NICOLAUS IWANOV (*Chem. Zentr.*, 1912, ii, 1384—1385; from *Zeitsch. Garüngsphysiol. Mykologie*, 1912, 1, 230—252).—The action of antiproteolytic by-products in yeast fermentation may be overcome by the addition of acid phosphates. Experiments with dead yeast cells (hefanol) show that the decomposition of albumin increases with the concentration of potassium dihydrogen phosphate, and that this increase is independent of temperature. By decreasing the volume of liquid, or by the addition of autolysis products, the action is still further increased, whereas leucine and tyrosine do not influence the process, but dipotassium hydrogen phosphate hinders it.

The proteolytic enzyme may be partly extracted from hefanol by means of water. When heated to 80°, it becomes inactive, but the addition of potassium dihydrogen phosphate revives its activity. It

seems that this salt is able to regenerate the peptase and to promote its action. J. C. W.

Comparative Influence of Potassium, Rubidium, and Cæsium on the Development and Sporulation of Aspergillus niger. BENJAMIN SAUTON (*Compt. rend.*, 1912, 155, 1181—1183).—*Aspergillus niger* was cultivated on Raulin's liquid in the presence of equivalent amounts of potassium, rubidium, and cæsium as chlorides, and the crops weighed after four days at 37°. Potassium causes an enormous increase in the crop, which is diminished by 50% on replacing the potassium by rubidium, whilst cæsium is not a nutrient substance for the organism. In a mixture of the chlorides, *Aspergillus niger* fixes the potassium before the rubidium and cæsium, thus forming a means of freeing the two latter from the last traces of the former metal. Potassium plays an important part in the sporulation, although in the absence of zinc this could not be conclusively demonstrated. On substituting rubidium or cæsium for potassium no spores are formed. W. G.

The Scission of a- and β-Methylglucoside by Aspergillus niger. ARTHUR W. DOX and RAY E. NEIDIG (*Biochem. Zeitsch.*, 1912, 46, 397—402).—*Aspergillus niger* acts on the two glucosides in exactly the opposite way to that in which yeast acts, for it readily hydrolyses the β-form (100% within six days), whereas it acts only slowly on the a-form, hydrolysing only 8% in twenty days. No capacity of adaptation of the ferment to the a-form could be demonstrated. S. B. S.

The Behaviour of Moulds (Aspergillus niger and Penicillium crustaceum) towards Phytin. M. A. JEGOROV (*Zeitsch. physiol. Chem.*, 1912, 82, 231—242).—The moulds mentioned grow well in a solution of phytin, and assimilate its phosphorus, especially in the presence of sucrose and peptone or glycerol. They split off phosphoric acid in high measure from the phytin. W. D. H.

Decomposition of Carbamide, Uric Acid, Hippuric Acid, and Glycine by Moulds. ALEXANDER KOSSOWICZ (*Bied. Zentr.*, 1912, 41, 791—792; from *Zeitsch. Garüngsphysiol. Mykologie*, 1912, 1, 60—60). —Pure cultures of the following moulds were found to assimilate urea, uric acid, hippuric acid, and glycine under sterilised conditions: *Botrytis lassiani*, *Aspergillus niger*, *Isaria farinosa*, a *Fusisporium*, *Mucor Boidin*, and *Phytophthora infestans*. *Penicillium brevicaule* and *P. crustaceum* utilise urea, uric acid, and glycine, whilst *Cladosporium herbarum* and *Aspergillus glaucus* only utilised urea and uric acid as sources of nitrogen. N. H. J. M.

The Apparent Respiration of Dead Cells in the Reduction of Pigments. OTTO MEYERHOF (*Pfluger's Archiv*, 1912, 149, 250—274).—Neutral and weakly alkaline acetone yeast possesses a measurable power of taking up oxygen, and this is increased in the presence of methylene-blue. In the presence of dead cells, reduction

of methylene-blue occurs also, but it occurs also if the dead cells are absent. It is, therefore, not due to anything of the nature of vitality. In one living animal cell, the egg of the sea-urchin, dissolved oxygen is present.　W. D. H.

The Action of Uranium on the Plant Cell. C. ACQUA (*Chem. Zentr.*, 1912, ii, 1471 ; from *Arch. Furmacol. sperim.*, 1912, 14, 81—84).—Dilute solutions of uranium salts (1 : 20,000 to 1 : 40,000) are absorbed by the cells of the roots of higher plants, where they hinder the division of the nuclei, and, consequently, the growth. The cells of the green parts are less permeable to uranium salts, and are therefore scarcely injured. Thorium and manganese salts have a similar but much smaller effect.　J. C. W.

Absorption of Aniline Dyes in Living Plant Cells. E. KUSTER (*Bied. Zentr.*, 1912, 41, 763—764; from *Jahrb. wiss. Bot.*, 1911, 50, 261).—It is shown that a considerable number of dyes, insoluble in fats, are abundantly taken up by plant cells. Overton's lipoid hypothesis regarding the nature of the outer layer of protoplasm is, therefore, insufficient, whilst Ruhland's opinion that there is no relation between the diffusibility of dyes and their penetration into plant cells is incorrect.　N. H. J. M.

The Physical Character of Bio-electrical Differences of Potential. REINHARD BEUTNER (*Biochem. Zeitsch.*, 1912, 47, 73—93). —The difference of potential at the contact surfaces—part of plant/aqueous solution of an electrolyte—can be altered in the sense that increasing dilution of the electrolyte makes the solution more positive. The change can be expressed by the following equation:

$$\text{Pot. diff. } 1 - \text{Pot. diff. } 2 = 58 \log \frac{c_1}{c_2} - 58 \log \frac{1 + \sqrt{1 + 10^6 m^2 c_1{}^2}}{1 + \sqrt{1 + 10^6 m^2 c_2{}^2}}$$

where

$$\log \frac{1}{m} = \frac{\text{Limiting value of potential difference} - \text{Pot. diff. for } c = n/500}{58}.$$

The method of arriving at these equations is given, and also an experimental verification of the same. The biological significance is also discussed.　S. B. S.

Sterile Cultures of a Higher Plant. Assimilation of Nitrogen as Ammonia and as Nitrates. IVAN SCHULOV (*J. exper. Landw.*, 1912, 13, 200—205 (in Russian), 205—206 (German Abstr.). Compare Hutchinson and Miller, A., 1909, ii, 923).—The results of sand culture experiments, under sterilised conditions, showed ,that nitrogen in the form of ammonium sulphate is assimilated by maize plants. It is also shown that the availability of phosphorite is considerably increased by the employment of ammonium nitrate, and that ammonium nitrate overcomes the injurious action of ammonium sulphate.
N. H. J. M.

Localisation and Function of Potassium in Plants. TH. WEEVERS (*Bied. Zentr.*, 1912, 41, 764—765 ; from *Rec. trav. bot. Néerland.*, 1911, 8, 289—332).—By means of Macallum's reagent

(sodium cobaltinitrate with ammonium sulphide and glycerol) it was found that potassium is present in all parts of *Thallophytes*, whilst negative results were obtained with the pollen grains of crocus and tulips. The greatest amount of potassium in *Phanerogams* was found in the young, embryonal tissues rich in plasma, and in the parenchyma of leaves, seeds, roots, and stems.

The conclusion is drawn that potassium takes part in the production of proteins. Its absence in the chlorophyll is opposed to the theory of Grafe and Stoklasa, that it takes part in the process of assimilation.   N. H. J. M.

Chlorogenic and Saccharic Acids in Latex. K. Gorter (*Rec. trav. chim.*, 1912, 31, 281—286).—The colour reactions with ferric chloride which de Jong and Tromp de Haas (A., 1904, ii, 762) have shown to be characteristic of the latex of certain plants resemble the reactions with the chlorogenic acid obtained from coffee (A., 1908, i, 186). A delicate test for this acid is now described. It consists in boiling the suspected substance with dilute hydrochloric acid for an hour, extracting with ether, and shaking the washed and not too concentrated extract with very dilute ferric chloride, when a violet coloration is produced. By this means it is shown that chlorogenic acid is present in the latex of *Ficus elastica* and of *Castilloa elastica*. It has actually been isolated from the latter substance, 300 grams of the latex yielding 0·3 gram chlorogenic acid, m. p. 208°, $[a]_D^{25} - 35·2°$. The latex of *Ficus elastica* contains, in addition, an organic magnesium salt, which has now been isolated and given the formula

$$C_6H_8O_8Mg,3H_2O.$$
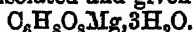
The free acid has $[a]_D^{25} + 36·5°$, and gives a sparingly soluble potassium salt, which closely resembles potassium disaccharate, and a diphenylhydrazone, m. p. 210°, which is identical with that derived from *d*-saccharic acid. This magnesium salt is the first indication of the occurrence of *d*-saccharic acid in nature.   J. C. W.

The Carboxylase of Higher Plants. W. Zaleski and Elisabeth Marx (*Biochem. Zeitsch.*, 1912, 47, 184—185).—Neuberg has shown that yeast can ferment pyruvic acid with evolution of carbon dioxide. The authors now show that the addition of this acid to powdered pea-seeds causes an increase of the post-mortal production of carbon dioxide, which takes place with equal energy in air and hydrogen.   S. B. S.

Basic Constituents of Fly Agaric. E. Buschmann (*Chem. Zentr.*, 1912, ii, 613; from *Pharm. Post*, 1912, 45, 453—454).—A methyl alcohol extract of fly agaric (*Amanita muscaria*) by precipitation with phosphotungstic acid and silver nitrate yielded hypoxanthine and xanthine, the former predominating (compare Zellner, *Chemie der höheren Pilze*, 1907).   T. A. H.

The Inulin Metabolism of Cichorium Intybus (Chicory). II. The Formation and Storage of Inulin. Viktor Grafe and V. Vouk (*Biochem. Zeitsch.*, 1912, 47, 320—330. Compare A., 1912, ii, 977).—From estimations of reducing sugar and inulin in different

parts of the plant collected at different periods, the following conclusions were drawn.   The inulin is not merely a reserve material, but is intimately connected with the general carbohydrate metabolism, as it can be readily detected macrochemically in the parenchymatous cells of the leaves of young plants.   No difference in the inulin and lævulose content of leaves of plants collected in the morning and afternoon could be detected.   From this fact the conclusion is drawn that new carbohydrate is formed during the day in such quantity that an equilibrium is maintained between the lævulose and inulin.   As the development of the root progresses there is a constant increase in the inulin content, accompanied at first by a diminution of the lævulose ; the latter increases in quantity again as the roots ripen.

S. B. S.

The Organic Phosphoric Acid of Cotton-seed Meal.   R. J. ANDERSON (*J. Biol. Chem.*, 1912, 13, 311—324).—The organic phosphorised substance from cotton-seed meal is probably either phytin or an isomeride ; this is to be ascertained by further work.

W. D. H.

Pigments of the Fucoideæ.   HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1912, 82, 221—230).—The fucoideæ contain carrotene and a crystalline, yellow pigment probably identical with xanthophyll.   They further contain a yellow pigment, phycoxanthin, which differs from xanthophyll in being soluble in light petroleum.   E. F. A.

Presence of Gentiopicrin, Gentianose, and Sucrose in the Fresh Roots of Gentiana Asclepiadea.   MARC BRIDEL (*Compt. rend.*, 1912, 155, 1164—1166).—The author has isolated and characterised gentiopicrin, gentianose, and sucrose from the fresh roots of *Gentiana Asclepiadea*, and has obtained indications of the presence of another carbohydrate, hydrolysable by invertin.   W. G.

The Constituents of Ipé tabaco Wood (Bignonia tecoma). OTTO A. OESTERLE (*Chem. Zentr.*, 1912, ii, 1666—1667 ; from *Schweiz. Woch. Chem. Pharm.*, 1912, 50, 529—532).—In order to investigate the nature of Lee's tecomin (T., 1901, 79, 284), the alcoholic extract of *B. tecoma* wood has been freed from resinous matter by means of benzene and light petroleum, leaving a mixture which was partly soluble in boiling sodium carbonate solution.   The soluble substance crystallised in yellow needles or leaflets, m. p. 142—143°, soluble in alkalis and alkali carbonates with intense red colours which disappeared on reduction, but soon reappeared in the air.   Tecomin is possibly identical with lapachol.   From the substance which remained undissolved by sodium carbonate, light yellow needles, m. p. 242°, were obtained.   J. C. W.

Variations of the Fatty Matters, Sugars, and Saponin during the Maturation of Seeds of Lychnis Githago.   (Mlle.) MARIE KORSAKOV (*Compt. rend.*, 1912, 155, 1162—1164).—The fatty matters, sugars, and saponin have been estimated in the seeds of *Lychnis Githago*

at three stages in their development: (*a*) just after flowering, when young and white; (*b*) further advanced but still white; (*c*) almost ripe and black. The results show a marked decrease in the content of fatty matters and sugars, reducing and non-reducing, and an increase in the saponin content with advance in development. The young seeds only contain traces of saponin, and the amount of saponin in the other organs of the plant being practically nil, it seems that the glucoside must be formed in the seed itself.   W. G.

Presence of Gentiopicrin in Swertia perennis. MARC BRIDEL (*Compt. rend.*, 1912, 155, 1029—1031; *J. Pharm. Chim.*, 1912, [vii], 6, 481—484).—*Swertia perennis* contains the glucoside gentiopicrin, which can be isolated in the pure state and hydrolysed by emulsin (compare Bourquelot and Bridel, A., 1910, ii, 234) There are also indications of the presence of a carbohydrate, which is only very slowly hydrolysed by emulsin.   W. G.

Occurrence of Trehalose, Vanillin, and *d*-Sorbitol. EDMUND O. VON LIPPMANN (*Ber.*, 1912, 45, 3431—3434).—After exposure to a sudden sharp frost in July, the flowers of some blooming rushes, *Carex brunescens*, growing in a sheltered spot, were observed to be covered with minute, hard, white crusts, which proved to be hydrated trehalose, $C_{12}H_{24}O_{11},2H_2O$.

The flowers of an orchid, *Gymnadenia albida*, growing last summer on the heights above Davos, were observed by the author to have a strong odour of vanilla; vanillin was isolated from them. Under normal conditions of growth, the flowers of this orchid contain little or no vanillin.

During last year's wet summer, many fungi in the fields near Kissingen grew in enormous quantities and to prodigious size, in particular, a variety of *Boletus bovinus*, which reached the dimensions of a dinner plate. After fine weather had set in, a number of the tops of these fungi, which had been struck off by a passer-by and had partly dried, were found to be covered with a network of a crystalline substance which on examination proved to be hydrated *d*-sorbitol.

                                                    C. S.

Chemical means of Protecting Plants from Frost. N. A. MAXIMOV (*Ber. Deut. bot. Ges.*, 1912, 30, 504—416. Compare A., 1912, ii, 476).—The supposition that the protective action of the substances employed depends on the eutectic point of the solution is confirmed by the results of further experiments in which mixtures instead of single substances were used. A mixture of mannitol and potassium nitrate considerably increased the power of resisting cold, whilst the two substances, singly, have very little effect.

As regards the connexion between the protective action and the permeability of the plasma for the protective substance, it is now shown that the action takes place immediately, and that the result depends on the action of the solution on the surface of the plasma. From this it follows that the death of plants by freezing is due to injury to the surface of the plasma.   .   N. H. J. M.

Alfalfa. IV. **Enzymes Present in Alfalfa Seeds.** C. A. JACOBSON (*J. Amer. Chem. Soc.*, 1912, **34**, 1730—1740).—In continuation of the investigation of alfalfa (*Medicago sativa*) (A, 1912, ii, 80, 239, 976), a study has been made of the enzymes contained in the seeds. The results show that the seeds contain enzymes, which, like amylase and emulsin, are capable of hydrolysing starch and amygdalin respectively; an enzyme which coagulates milk, like rennin; an enzyme, which like the peroxydases, precipitates purpurogallin from a pyrogallol solution containing hydrogen dioxide, and an enzyme, resembling proteases in being able to digest casein and Witte peptone. This protease is found to be a vegetable erepsin, since it will not begin the digestion of egg-albumin, blood-serum, legumin, or conglutin, and its digestion of casein and Witte peptone is checked to some extent by the presence of egg-albumin or blood-serum. The seeds do not appear to contain invertase or lipase.   E G.

Comparative Efficiency for Growth of the Total Nitrogen from Alfalfa Grass and Corn Grain. EDWIN B. HART, GEORGE C. HUMPHREY, and F. B. MORRISON (*J. Biol. Chem.*, 1912, **13**, 133—154). —Experiments on heifers show that the utilisation of nitrogen for growth is as efficient when the source is alfalfa hay as when it is corn kernel. There was no sudden increase or decrease in the nitrogen of urine or fæces when the animals were suddenly changed from one ration to the other. The amide-nitrogen, which is high in the grass, is therefore not valueless. The effect on milk production will be treated later. In growing heifers, the creatinine output rises with increased storage of nitrogen.   W. D. H.

Observations on the Action of Fluorine in Nature. UGO ALVISI (*Gazzetta*, 1912, **42**, ii, 450—452).—The author confirms the presence of fluorine in wheat (when ripe) and in human teeth. He suggests the employment of calcium silicofluoride as a manure.
                                                                    R. V. S.

Reducing Substances Present in Fresh Sugar Beets. Their Influence on the Direct Estimation of Sucrose in the Beet. HENRI PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1912, **30**, 239—253).— Freshly harvested sugar beets always contain a small quantity of reducing sugar, amounting to 0·05—0·27 gram per 100 c.c. of the sap. This amount is independent of the initial richness of the beet in sucrose, and does not vary in different parts of the same beet. The estimation is made in the sap clarified by treatment with neutral lead acetate; basic lead acetate precipitates some of the reducing sugar. Beets of inferior quality contain 2—2·5 grams of reducing sugar per 100 c.c of sap. Beets stored in silos lose some of their sucrose, but the amount of reducing sugar does not increase. Beets damaged during harvesting or transport contain 0·3—0·35 gram of reducing sugar; in sickly beets the quantity increases to 0·4—0·5 gram per 100 c.c. of sap.

Reducing sugar is not formed during diffusion. The amount arising

during the processes of manufacture is very small when proper care is exercised.

The presence of this reducing sugar renders the polarimetric estimation of the sucrose in the beet-juice inaccurate.   E. F. A.

Sesame Cake. ACH. GRÉGOIRE and EM. CARPIAUX (*Bull. Soc. chim. Belg.*, 1912, **26**, 479—485).—A number of samples of sesame cake have been examined with respect to the content of pure ash, lime, fat, acidity of fat, and oxalic acid. The results show great variations in the composition of the commercial products.

The pure ash contains, as a mean value, 34·5% of lime, the extreme values being 28·4% and 39·8% respectively. This determination may be employed for controlling the purity of sesame cake, since the great majority of other seeds yield an ash relatively poor in lime. Sesame cake, free from oil and earth, contains an average of 1·99% anhydrous oxalic acid, the individual determinations varying between 1·44% and 2·96%. This value is not sensibly altered when the oil becomes rancid. Free oxalic acid could not be detected.   H. W.

The Black Earths of the Valley of l'oued R'Dom in Morocco. G. GIN (*Compt. rend.*, 1912, **155**, 1166—1167).—An account of a black arable earth from a fertile valley traversed by l'oued R'Dom. A description of the earth and results of chemical analyses are given. It is found to support vegetation even in the warm, dry months, and this is supposed to be due to the presence of a trihydrated aluminium oxide in the clay, which supplies the necessary water during the dry months, and recoups itself at the next wet season. The black colour is due to an amorphous humic substance, which is partly soluble to a brown solution in potassium hydroxide.
          W. G.

Agronomic Study of Manganese. P. NOTTIN (*Compt. rend.*, 1912, **155**, 1167—1169).—A study of the behaviour of different soils towards soluble manganese salts. Soil has the power of rendering the manganese insoluble and fixing it, the constituents of the soil, however, having different absorbent powers. Silica and humus play no part in the manganese fixation. Chalk produces fixation of the manganese by interchange of the calcium and manganese. Natural clay also has a marked absorbent power, independent of the lime present.
          W. G.

Nitrolim and its Decomposition in the Soil. III. C. J. MILO (*Chem. Zentr.*, 1912, ii, 1393; from *Med. Proefstat. Java-Suikerind*, 1912, 601—634. Compare A., 1912, i, 16).—Nitrolim is hygroscopic, and absorbs water and carbon dioxide with liberation of nitrogen. The calcium cyanamide decomposes into cyanamide and carbamide, which, with the help of micro-organisms, gives rise to ammonium carbonate. In soils which are only slightly absorptive, the calcium cyanamide gives basic salts and cyanamide, and further decomposition proceeds very slowly.   J. C. W.

Organic Chemistry.

Purification of Saturated Hydrocarbons by means of Potassium Permanganate. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1748—1753).—Saturated hydrocarbons, when prepared by the reduction of their halogen derivatives, are usually contaminated with unsaturated hydrocarbons, and the same is the case with trimethylenic hydrocarbons prepared by Gustavson's method. The removal of these impurities is an easy matter when the saturated hydrocarbons are stable to concentrated sulphuric acid or to fuming nitric acid; but in some cases the unsaturated hydrocarbons are converted into saturated ones by these reagents, and in certain others the carbonatom skeleton undergoes isomerisation.

The author has investigated the efficacy of potassium permanganate as a means of purification in these exceptional instances. The results show that the complete removal of small admixtures of the unsaturated compounds in this way is very difficult, and is accompanied by the loss of much of the saturated hydrocarbons. As the concentration of the unsaturated hydrocarbon in the mixture diminishes, its rate of oxidation decreases, until finally it may become less than that at which the saturated compound oxidises; thus a mixture containing 15 parts of menthane and 5 parts of menthene is converted into one containing 11·5 and 2·5 parts respectively by one oxidation, these amounts becoming 7·2 and 0·8, and 3·7 and 0·3 after successive oxidations. Somewhat similar results are obtained with mixtures of menthane and limonene.   T. H. P.

Fractional Distillation of Coal. LÉO VIGNON (*Compt. rend.*, 1912, 155, 1514—1517).—The author has distilled various samples of coal at successive temperatures of 400°, 600°, 850°, 1000° and 1200°, and analysed the gaseous mixtures evolved at these temperatures. The results show (1) that the unsaturated hydrocarbons (acetylene, ethylene, etc.) almost all pass over below 600° and disappear entirely at higher temperatures; (2) methane and its homologues are very abundant (60—80% of total gas) up to 800°, after which they decrease rapidly with rise in temperature; (3) from 800—1000° hydrogen predominates, but in its turn diminishes above 1000°; (4) very high temperatures favour the formation of carbon monoxide.

Rise in distillation temperature produces an increase in the total volume of gas evolved, but a diminution in its calorific power.
                                                                 W. G.

A New Method for Determining the Position of the Double Bond. JOH. JEGOROV (*J. pr. Chem.*, 1912, [ii], 86, 521—539).—The method consists in combining the unsaturated compound with nitrogen peroxide, and heating the resulting additive compound with concentrated hydrochloric acid, whereby the molecule becomes ruptured at the position originally occupied by the double linking with the forma-

tion of two carboxylic acids : $R \cdot CH \colon CHR^1 \longrightarrow NO \cdot O \cdot CHR \cdot CHR^1 \cdot NO_2$, or $NO_2 \cdot CHR \cdot CHR^1 \cdot O \cdot NO \longrightarrow R \cdot CO_2H + R^1 \cdot CO_2H$.

The transformation of a nitrite into a carboxylic acid has been investigated in the case of amyl nitrite, which, under the influence of hydrochloric acid, yields amyl alcohol and an ester, presumably amyl valerate, the valeric acid being formed by the oxidising action of the nitrite on the amyl alcohol.

When heated with water at 160—170°, the light yellow, oily, additive compound of oleic acid and nitrogen peroxide yields pelargonic acid, ω-*nitrononane*, azelaic acid, and θ-*nitrononoic acid*. The nitro-compounds could not be isolated in a state of purity, and therefore were identified by reducing them to the corresponding amino-compounds.

θ-*Aminononoic acid*, $NH_2 \cdot CH_2 \cdot [CH_2]_7 \cdot CO_2H$, was isolated in the form of its *platinichloride* from the above mixture by distillation in steam, and reduction of the residual nitrononoic and azelaic acids with tin and hydrochloric acid.

Nonylamine is a viscid liquid, and forms a *hydrochloride* which becomes black when heated without showing a definite m. p.; the *platinichloride*, $2C_9H_{19} \cdot NH_2, H_2PtCl_6$, crystallises in golden-yellow needles.

When heated with concentrated hydrochloric acid, the additive compound of oleic acid and nitrogen peroxide yields pelargonic and azelaic acids, together with hydroxylamine.

From these results the conclusion is drawn that the additive compound consists of a mixture of two isomerides (I) and (II), which, when heated with water, undergo the transformations shown in the following scheme :

(I.) $2C_8H_{17} \cdot CH(NO_2) \cdot CH(O \cdot NO) \cdot C_7H_{14} \cdot CO_2H \longrightarrow H_2O + N_2O +$

    $2C_8H_{17} \cdot CH(NO_2) \cdot CO \cdot C_7H_{14} \cdot CO_2H \xrightarrow{H_2O} C_9H_{19} \cdot NO_2 + C_7H_{14}(CO_2H)_2$.

(II.) $2C_8H_{17} \cdot CH(O \cdot NO) \cdot CH(NO_2) \cdot C_7H_{14} \cdot CO_2H \longrightarrow H_2O + N_2O +$
$C_8H_{17} \cdot CO \cdot CH(NO_2) \cdot C_7H_{14} \cdot CO_2H \longrightarrow C_8H_{17} \cdot CO_2H + NO_2 \cdot C_8H_{16} \cdot CO_2H$.
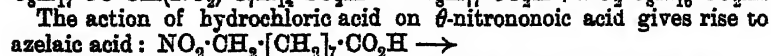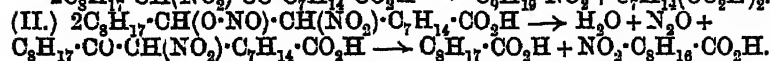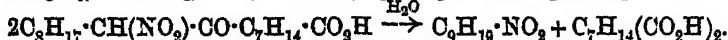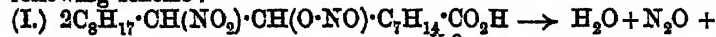
The action of hydrochloric acid on θ-nitrononoic acid gives rise to azelaic acid : $NO_2 \cdot CH_2 \cdot [CH_2]_7 \cdot CO_2H \longrightarrow$
    $HO \cdot N \colon C(OH) \cdot [CH_2]_7 \cdot CO_2H \longrightarrow NH_2 \cdot OH + C_7H_{14}(CO_2H)_2$.
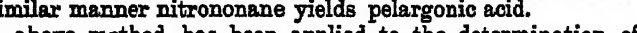
In a similar manner nitrononane yields pelargonic acid.

The above method has been applied to the determination of the position of the double linking in a number of unsaturated compounds. In all cases the unsaturated compound was allowed to combine with nitrogen peroxide in light petroleum solution at a low temperature, and the resulting oily additive compounds were heated with concentrated hydrochloric acid at 130—140°.

Undecenoic acid gave sebacic and formic acids. *iso*Oleic acid decomposes into octoic and sebacic acids, corresponding with the structure $CH_2Me \cdot [CH_2]_5 \cdot CH \colon CH \cdot [CH_2]_8 \cdot CO_2H$; erucic acid into nonoic and brassylic acids.

From the behaviour of the hexylene, prepared from mannitol, which yielded formic, acetic, butyric and valeric acids, the author draws the conclusion that the hydrocarbon consists of a mixture of two isomerides, $CHMe \colon CHPr^a$ and $CH_2 \colon CH \cdot CH_2Pr^a$.

Methoxy- and ethoxy-undecenoic acids, obtained by the action of alcoholic alkali hydroxides on the dibromide of undecenoic acid, gave results in agreement with the structure:

$$OMe \cdot CH_2 \cdot [CH_2]_7 \cdot CH:CH \cdot CO_2H.$$
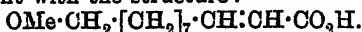
The unsaturated acids from linseed oil were also examined and found to consist of a mixture of the two following compounds:

$$CHEt:CH \cdot CH_2 \cdot CH:CH \cdot CH_2 \cdot CH:CH \cdot [CH_2]_7 \cdot CO_2H.$$
$$CH_3 \cdot [CH_2]_4 \cdot CH:CH \cdot CH_2 \cdot CH:CH \cdot [CH_2]_7 \cdot CO_2H.$$
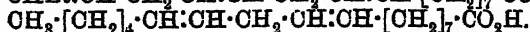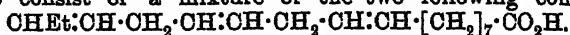
F. B.

The Theory of the Asymmetric Carbon Atom and Pasteur's Principle. ERNST MOHR (*J. pr. Chem.*, 1912, [ii], 87, 91—95).—A theoretical · paper in which the author shows that, contrary to his previous views (A., 1904, i, 1), a compound of the formula $C(dR)_2(lR)_2$, where dR and lR represent structurally identical, univalent groups of enantiomorphous configuration does not contain an asymmetric carbon atom, and is therefore incapable of existing in two enantiomorphous forms. F. B.

The Melting Point of Ethylene Dibromide. EUGEN VON BIRON ·(*Zeitsch. physikal. Chem.*, 1913, 81, 590).—Moles (A., 1912, ii, 533) states that ethylene dibromide has m. p. 9·975°. Biron has shown that when purified by repeated fractional crystallisation it has m. p. 10·012° and D_4^{20} 2·1804 (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1609). He points out that the work must be carried out in the absence of light. J. F. S.

The History of Distillation and of Alcohol. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1913, 37, 1—2. Compare A., 1912, i, 824).—The author combats the statement attributed to Davidsohn (*Mitt. Ges. Med. Naturwiss.*, 1912, 12, 102) that the Celts first submitted fermented liquors to distillation and that the knowledge of the process passed from them to other nations. D. F. T.

Ethyl Ether by Catalysis. CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1913, 35, 93—96).—Sabatier and Mailhe (A., 1910, i, 294) have shown that several metallic oxides, including that of thorium, exert a catalytic action on alcohols between 300° and 350°. In the case of ethyl alcohol, the action appears to consist almost entirely of dehydration with formation of ethylene, but at a lower temperature the dehydration is said to be capable of limitation to the production of ether.

Experiments are described in which alcohol vapour was passed over pure thorium oxide at about 250°, but although the conditions specified by Sabatier and Mailhe were carefully observed, little or no ether was obtained. E. G.

Esters and Amides of the Phosphoric Acids. IV. Reaction between Esters of Metaphosphoric Acid and Uni- and Multivalent Alcohols. Synthesis of Glycero-mono- and -diphosphoric Acid. Preparation of Pure Silver Metaphosphate. KURT LANGHELD, F. OPPMANN, and E. MEYER (*Ber.*, 1912, 45, 3753—3760).—In part polemical (compare Grün and Kade, this vol.,

i, 159). When ethyl metaphosphate reacts with ethyl alcohol and benzyl alcohol, the following three products are formed :

$$PO(OEt)_2 \cdot O \cdot C_7H_7, \quad PO(OH)_2 \cdot O \cdot C_7H_7, \quad OEt \cdot PO(O \cdot C_7H_7) \cdot OH.$$
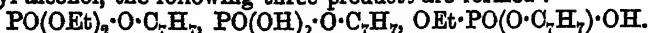
The mono- and tri-esters are obtained in molecular proportions. The same result is obtained with glycerol, in which case the excess prevents the determination of the relative proportions of the esters.

Barium glycerophosphate is obtained in stellar aggregates of small platelets containing a molecule of water, which is slowly removed on drying in a vacuum. On exposure of the anhydrous substance, $\frac{1}{2}H_2O$ is absorbed quickly and the second $\frac{1}{2}H_2O$ only slowly. The solubility in water at $220°$ is 8.4%, and approaches that of the natural product. *Barium glycerodiphosphate*, $2H_2O$, crystallises well.

To prepare pure silver metaphosphate, $(AgPO_6)_2, H_2O$, sodium ammonium phosphate is converted into metaphosphate by cautious heating in a vacuum at $320°$. About half the product is soluble in water, from which it is precipitated in crystalline form on the addition of alcohol. This product, $2NaPO_3, H_2O$, reacts with silver nitrate.

Silver metaphosphate crystallises in large octahedra. E. F. A.

The Glycerotriphosphoric Acid of Contardi. PAUL CARRÉ (*Compt. rend.*, 1912, **155**, 1520—1521*).—A reply to Contardi (compare A., 1912, i, 743), in which the author maintains that the esterification of 1 mol. of glycerol with 3 mols. of phosphoric acid gives glycerodiphosphoric acid, $C_3H_5(PO_4H_2)_2 \cdot OH$, glycerophosphoric acid, and a di-ester of the form PO_4R_2H, about 50% of the phosphoric acid remaining unaltered and no glycerotriphosphoric acid being formed.

He further maintains his views, already expressed (compare A., 1904, i, 133, 215 ; 1905, i, 184), that, on heating an equimolecular mixture of glycerol and phosphoric acid in a vacuum, the mixture is transformed quantitatively into the normal tri-ester. W. G.

Crystalline Forms of Salts of Ethanedisulphonic Acid. K. BLEICHER (*Zeitsch. Kryst. Min.*, 1912, **51**, 502—520).—Detailed crystallographic constants are given for the following salts of ethanedisulphonic acid : Sodium $(2H_2O)$, monoclinic ;

$$a:b.c = 0.7893:1:0.4634;$$

$\beta = 91°34'$. Lithium $(2H_2O)$, monoclinic; $a:b:c = 1.5717:1:2.5939$; $\beta = 111°7'$. Potassium, monoclinic; $a:b:c = 1.2594:1:5816$; $\beta = 126°18'$. Ammonium, monoclinic; $a:b:c = 1.1647:1:0.6959$; $\beta = 120°21'$. Potassium sodium $(2H_2O)$, rhombic;

$$a:b:c = 0.7467:1:0.5563.$$

Disodium ammonium, $Na_4(NH_4)_2(C_2H_4S_2O_6)_3$, monoclinic; $a:b:c = 1.5637:1:0.5906$; $\beta = 101°17'$. Lithium potassium $(1H_2O)$, monoclinic; $a:b:c = 1.2401:1:1.2753$; $\beta = 104°41'$. Lithium ammonium, monoclinic; $a:b:c = 0.7627:1:0.7799$; $\beta = 96°46'$. Barium, rhombic; $a:b:c = 0.7678:1:0.9062$. Barium (H_2O), rhombic; $a:b:c = 0.9374:1:0.4051$. Strontium (H_2O), monoclinic;

$$a:b:c = 0.5347:1:0.0641;$$

$\beta = 101°3'$. Cadmium $(2H_2O)$, triclinic; $a:b:c = 1.7421:1:1.0515$; $a = 90°1'$, $\beta = 101°56'$, $\gamma = 100°54'$. Zinc $(3H_2O)$, triclinic; $a:b:c =$

$0.5718 : 1 : 0.7813$; $a = 94°0'$, $\beta = 110°28'$, $\gamma = 90°30'$. Magnesium ($4H_2O$), triclinic ; $a : b : c = 0.6546 : 1 : 0.4066$; $a = 96°18'$, $\beta = 102°9'$, $\gamma = 94°14'$. Copper ($4H_2O$), triclinic ; $a : b : c = 0.6527 : 1 : 0.4350 :$ $a = 95°15'$, $\beta = 96°39'$, $\gamma = 94°32'$. L. J. S.

Phenomenon of Double Melting for Fats. ANDREAS SMIT, and S. C. BOKHORST (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 681—683).—According to Guth (A., 1903, i, 225), tristearin melts at 71·5°, but if allowed to solidify in a capillary tube it melts at 55°, solidifies again, and melts a second time at 71·5°. In view of the improbable explanation of these results, the authors have made a further examination of the behaviour of the substance, and find that the above phenomena are due to the existence of two crystalline modifications. Of these, the metastable form appears most readily. If, however, the liquid is kept for some time at a temperature between the two melting points, the stable form crystallises out, although very slowly.

When the metastable form is heated, it melts at 54·5°, and when the temperature is then raised to 63° the stable form is deposited. The stable unary melting point is 70·8°. It is probable that the double melting phenomena, observed for other fats, are to be explained in the same way. H. M. D.

Anomalies in the Consistency and Melting Points of Fats. ADOLF GRÜN (*Ber.*, 1912, 45, 3691—3701).—It has already been observed that glycerides can exist in two modifications (Kast, A., 1906, i, 922 ; Grün and Schacht, A., 1907, i, 462). To this phenomenon is attributable the variation in the m. p. recorded for certain fats with the age or method of preparation of the sample. The present investigation endeavours to extend the present limited knowledge of this phenomenon.

[With A. CUSTODIS].—$a\gamma$-Dilaurin, obtained from $a\gamma$-dichlorhydrin and potassium laurate, is a mixture of two modifications ; the product of higher m. p., 57°, *acetyl* derivative, m. p. 34°, or after one year 32°, is obtained in better yield the lower the reaction temperature (140—150°), whilst the other modification, m. p. 40°, preponderates when the temperature of formation is somewhat higher (170—180°) ; the latter modification very easily remains in a supercooled condition. Both forms, on keeping, finally attain a m. p. 45°, which is also the temperature observed for a mixed m. p. It is probable that the two substances are structurally identical.

When the two forms of $a\gamma$-dilaurin are treated with lauryl chloride at 100°, two modifications of trilaurin are obtained, one m. p. 45°, the other forming soft needles which melt in the hand. The former, obtained from the less fusible dilaurin, is identical with natural trilaurin ; the latter, obtained from the more fusible dilaurin, resembles its parent substance in having in benzene a molecular weight only one-half that expected from the formula ; the less fusible di- and tri-laurins are of normal molecular weight.

$a\gamma$-Dibenzoin, $OBz \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OBz$, by warming with glycerol and sulphuric acid, can be converted into a modification

which remains oily at the ordinary temperature ; the molecular weight of the substance in benzene solution is, however, approximately normal.

$a\beta$-Dibenzoin, obtained from anhydrous potassium benzoate and $a\beta$-dibromohydrin, and al-o in a purer condition by the use of silver benzoate, is also a viscous, uncrystallisable oil.

In an addendum it is remarked that lack of recognition of the above peculiarities of glycerides may lead to considerable errors, as, for example, the reported formation of $a\beta$-dilaurin from $a\gamma$-dichlorohydrin (van Eldik Thieme, A., 1912, i, 333).   D. F. T.

The Synthesis of Fats. DAVID HOLDE (*Ber.*, 1912, 45, 3701—3702. Compare Kremann and Schoulz, A., 1912, ii, 1152).— The author draws attention to the manner in which the results of Kremann and Schoulz (*loc. cit.*) support his views (A., 1903, i, 140) that the stearic and palmitic acids in olive oil must be present in the form of " mixed " glycerides, and not as tripalmitin and tristearin.
                                                           D. F. T.

Diglyceride-phosphoric Acids. ADOLF GRUN and FRITZ KADE (*Ber.*, 1912, 45, 3358—3367).—When phosphoric oxide acts on distearin at temperatures above 100°, or in the absence of moisture, blackening takes place. When the requisite amount of water is added, esters of pyrophosphoric acid or primary orthophosphoric acid esters are obtained. The former decompose into phosphoric acid and the ortho-acid esters, which are transformed in turn into secondary and tertiary esters and finally into the stable form, pentadistearin phosphate. In addition the reaction product contains free phosphoric acid and distearin. The changes are expressed by the scheme :

$$PO(OR)(OH)\cdot O\cdot PO(OH)_2 \longrightarrow PO(OR)(OH)_2 \longrightarrow$$
$$PO(OR)_2(OH) \longrightarrow PO(OR)_3 \longrightarrow P(OR)_5.$$
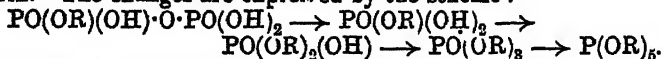
$a\beta$-*Distearin pyrophosphate*, $C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2\cdot O\cdot P_2H_3O_6$, is a colourless, crystalline, fatty substance, m. p. about 65°; primary $a\beta$-*distearin orthophosphate* forms colourless, somewhat lustrous, matted crystals, m. p. 71°. The *secondary* ester yields soft crystals, m. p. about 67°; it forms a waxy, pale yellow *silver* salt with silver acetate, and a *potassium* salt separating in colourless platelets. The *tertiary* ester is very similar to the other esters, but the solution is neutral.

Pentadistearin phosphate, $P[O\cdot C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2]_5$, forms colourless, brittle crystals, m. p. 70°. All the compounds described are very ill-defined.   E. F. A.

Alleged Synthesis of Lecithins. ADOLF GRÜN and FRITZ KADE (*Ber.*, 1912, 45, 3367—3376).—To effect the synthesis of lecithins it is proposed to allow the components of choline to act in turn on diglyceride-phosphoric acid. Ethylene glycol and phosphoric oxide acting on distearin produce almost quantitatively *distearin ethylene-glycol orthophosphate*,

$$C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2\cdot O\cdot PO(OH)\cdot O\cdot C_2H_4\cdot OH.$$
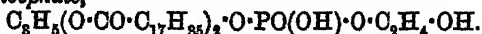
When ethylene chlorohydrin is used, the reaction takes place in two directions, the glycol ester as well as the β-*chloroethyl* ester,

$$C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2\cdot O\cdot PO(OH)\cdot O\cdot C_2H_4Cl,$$
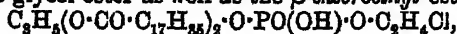
being formed. This compound reacts with trimethylamine, forming the *trimethylammonium* salt,

$$C_3H_5(O \cdot CO \cdot C_{17}H_{35})_2 \cdot O \cdot PO(O \cdot C_2H_4Cl) \cdot O \cdot NHMe_3,$$
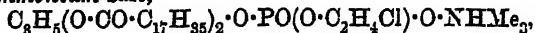
and on more energetic action of excess of trimethylamine this undergoes rearrangement to lecithin hydrochloride,

$$C_3H_5(O \cdot CO \cdot C_{17}H_{35})_2 \cdot O \cdot PO(O \cdot C_2H_4 \cdot NMe_3Cl) \cdot OH.$$
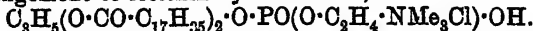
The final product obtained was a mixture of both compounds together with an intermediate product.

The *β-chloroethyl* ester, from *αβ*-distearinphosphoric acid, forms colourless crystals, which sinter at 60°, m. p. 65—66°; the isomeric *αγ*-distearin compound is very similar.

The *ethyleneglycol* ester of *αβ-distearinphosphoric* acid has m. p. 65—70°, and is a typically fatty substance. It reacts faintly acid.

The *trimethylammonium* salt forms tough crystals which sinter at 60°, m. p. 69°.

The synthetic lecithin hydrochloride (*αβ*-distearincholinephosphoric acid ester) product is a soft, waxy compound, which sinters at 60° to a clear, viscid oil, which becomes mobile at 64—65° and opaque at 74°.

E. F. A.

Preparation of Mixed *αβ*-Diglycerides. ADOLF GRUN and B. SCHREYER (*Ber.*, 1912, **45**, 3420—3426).—Glycerol-*α*-monochlorohydrin is converted by the action of myristoyl chloride into the ester, $CH_2Cl \cdot CH(OH) \cdot CH_2 \cdot O \cdot CO \cdot C_{13}H_{27}$, which reacts with stearyl chloride to form myristostearochlorohydrin,

$$CH_2Cl \cdot CH(O \cdot CO \cdot C_{17}H_{35}) \cdot CH_2(O \cdot CO \cdot C_{13}H_{27}).$$

On treatment with silver nitrite the chlorine atom is replaced by hydroxyl and *α*-myristo-*β*-stearin obtained.

α-Myristo-γ-chlorohydrin is a yellow, mobile oil; it is converted by silver nitrite into *α*-monomyristin, m. p. 68°.

β-Myristo-αγ-dichlorohydrin forms colourless, transparent, glass-like crystals, m. p. 20°. The *β-monomyristin* obtained from it gives colourless, lustrous, crystalline plates, m. p. 69°.

α-Myristo-β-stearo-γ-chlorohydrin forms colourless crystals, m. p. 31°.

α-Myristo-β-stearin crystallises in slender platelets, m. p. 58°.

E. F. A.

Alcoholysis and the Composition of Cocoanut Oil. GEORGE D. ELSDON (*Analyst*, 1913, **38**, 8—11).—Cocoanut oil when boiled in a reflux apparatus with absolute methyl alcohol containing 2% of hydrogen chloride for about twenty hours deposits on cooling a large quantity of methyl esters; the remainder may be obtained by diluting the alcoholic solution with water and agitating with ether.

When the mixture of the esters is submitted to distillation at 14 mm. pressure, seven fractions may be isolated (b. p. 63—76°, 76—100°, 100—128°, 128—153°, 153—182°, 182—204°, 204—216°).

From the results obtained on weighing, refractionating, and further identification of the fractions, the author considers that the composition of the fatty acids and of cocoanut oil may be represented approximately

by hexoic acid 2%, octoic acid 9%, decoic acid 10%, lauric acid 45%, myristic acid 20%, palmitic acid 7%, stearic acid 5%, and oleic acid 2%.

L. DE K.

Preparation of Ethyl Acrylate. FREDERICK G. TROBRIDGE (*Proc. Univ. Durham, Phil. Soc.*, 1912, **4**, 223—224).—Ethyl acrylate is obtained in 80% yield by the action of the zinc–copper couple on ethyl $\alpha\beta$-dibromopropionate in ethereal solution.   F. B.

Action of Zinc on a Mixture of Pinacolin and Ethyl α-Bromopropionate. NICOLAI N. BUNGE (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1776—1788).—This incomplete investigation is published owing to the appearance of Umnova's paper (this vol., i, 7), and is a continuation of work begun by Lazarkevitsch and proceeded with by Reformatski and Agafonov.

The products of the action of zinc on a mixture of pinacolin (1 mol.) and ethyl bromopropionate (1 mol.) vary with the conditions of the reaction. If the latter takes place at the ordinary temperature and the viscous mass obtained after three or four days is decomposed with water, a yield of 30% of ethyl β-hydroxy-$\alpha\beta\gamma\gamma$-tetramethylvalerate is obtained. At 50—70°, however, this ester is accompanied by (1) a lactone, $C_9H_{16}O_2$, which may also be obtained by boiling either the ester or the corresponding acid for some hours with 20% sulphuric acid solution ; (2) ethyl propionylpropionate, which yields diethyl ketone on hydrolysis.

β-*Hydroxy-$\alpha\beta\gamma\gamma$-tetramethylvaleric acid,*

$$CMe_3 \cdot CMe(OH) \cdot CHMe \cdot CO_2H,$$
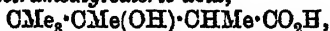
forms large, colourless crystals (? rhombohedra), m. p. 109·5—110·5°, and has the normal molecular weight in freezing acetic acid. Its *ethyl* ester, $C_{11}H_{22}O_3$, is a colourless, viscous liquid, b. p. 117°/20 mm., D_4^{20} 0·96034, n_D^{20} 1·44039, and exhibits normal cryoscopic behaviour in benzene. The *potassium, barium, calcium* ($+ H_2O$), and *silver* salts were analysed.
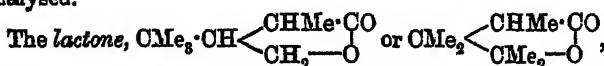
The *lactone,* $CMe_3 \cdot CH < \begin{smallmatrix} CHMe \cdot CO \\ CH_2 — O \end{smallmatrix}$ or $CMe_2 < \begin{smallmatrix} CHMe \cdot CO \\ CMe_2 — O \end{smallmatrix}$, forms large crystals, m. p. 65—66°, and exhibits the normal molecular weight in freezing acetic acid ; when boiled with water it yields a neutral solution and does not combine with it.   T. H. P.

Uranium Salts. ARRIGO MAZZUCCHELLI and OLGA GRECO D'ALCEO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 620—626).—The paper deals with complex uranium salts. Additive products are practically not formed in the following cases : mercuric cyanate, carbamide or thiocarbamide with uranyl nitrate ; carbamide or hexamethylenediamine with uranyl oxalate ; hexamethylenediamine, aniline or pyridine with the complex sodium uranyl pyrophosphate, malonate or succinate. Attempts to prepare complex salts from aminoacetic, aspartic, aminobenzoic and sulphanilic acids were unsuccessful. The *aspartate,*

$$UO_2(C_4H_5O_4N)_2,3H_2O,$$

was prepared, but it is not a complex derivative. The *aminobenzoate,* $UO_2(C_7H_6O_2N)_2,4H_2O$, was obtained, and also the basic *sulphanilate,* $UO_2 \cdot C_6H_7O_3NS,H_2O$.

The uranous salts also appear to have little tendency to form aminic

complexes. Diurano-oxalic acid gives ordinary *salts* with *pyridine* $[2U(C_2O_4)_2 \cdot C_2O_4(C_5H_5N)_2]$ and with *aniline* $[2U(C_2O_4)_2 \cdot C_2O_4(C_6H_7N)_2]$. Indications were obtained of the formation of a complex salt in the case of uranous aminoacetate. The basic *succinate*, $UO \cdot C_4H_4O_4, 2H_2O$, was prepared, and also the analogous *malonate*, $UO \cdot C_3H_2O_4, 6H_2O$. When a solution of sodium uranylmalonate with an excess of malonic acid is electrolytically reduced, the anodic liquid being an acid solution of sodium malonate separated from it by a parchment, dark green, dichroic crystals of the complex *salt*, $U(C_3H_2O_4)_2Na_2, 2H_2O$, are obtained on subsequent concentration of the cathodic liquid in a vacuum. A basic *uranous phthalate*, $UO:C_8H_4O_4, 3H_2O$, and *uranous trichloroacetate*, $UO \cdot C_2O_2Cl_3)_2, 3H_2O$, were also prepared.

R. V. S.

Molecular Rearrangements in the Camphor Series. XI. Derivatives of *iso*Camphoric Acid : *iso*Aminocamphonanic Acid and Its Decomposition Products. WILLIAM A NOYES and LEONIDAS R. LITTLETON (*J. Amer. Chem. Soc.*, 1913, **35**, 75—81). —It has been shown in earlier papers (A., 1895, i, 295 ; 1909, i, 133) that aminocamphonanic acid (aminolauronic acid) is decomposed by nitrous acid with formation of lauronolic acid, laurolene, and *iso*-campholactone. The present work was undertaken with the object of preparing *iso*aminocamphonanic acid and studying its behaviour with nitrous acid.

sec.-Methyl *iso*camphorate (α-methyl *iso*camphorate),
$$CO_2H \cdot C_8H_{14} \cdot CO_2Me,$$
has m. p. 89·5—90°, and $[\alpha]_D - 58·4°$ in 10% alcoholic solution (compare Noyes and Knight, A., 1911, i, 111). The tert.-*methyl* ester, prepared by boiling a solution of the dimethyl ester in methyl alcohol with sodium hydroxide, was obtained as a very viscous oil ; it has $[\alpha]_D - 53·1°$ in 10% alcohol solution. The terms "secondary" and "tertiary" are used here to indicate the carboxyl containing the methyl group.
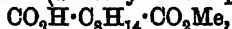
Methyl sec.-*isocamphoramate*, $CO_2Me \cdot C_8H_{14} \cdot CO \cdot NH_2$, m p. 126—127°, prepared from the *sec.*-methyl ester by converting it into the chloride and treating the latter with ammonia, crystallises in rectangular plates, and has $[\alpha]_D - 54·1°$ in 10% solution in methyl alcohol. When this ester is warmed with sodium hypobromite solution it yields *methyl* iso*aminocamphonanate*, b. p. 239° (corr.), m. p. 230° (decomp.), which forms white crystals ; the *hydrochloride*,
$$CO_2Me \cdot C_8H_{14} \cdot NH_2, HCl, H_2O,$$
has $[\alpha]_D - 32·03°$ in 10% solution in water, and $- 42·03°$ in 10% solution in alcohol. If this hydrochloride is warmed with solution of sodium hydroxide and subsequently acidified with hydrochloric acid, the *hydrochlo ide* of isoaminocamphonanic acid,
$$\begin{array}{c} CH_2-CH_2 \\ NH_2 \cdot CH \cdot CMe_2 \end{array}\!\!\!>CMe \cdot CO_2H, HCl,$$
m. p. 320° (corr.), is obtained, which is decomposed by nitrous acid with formation of *cis*-camphonolactone, together with small quantities of an unsaturated *acid*, b. p. 150°/60 mm. (decomp.), and a saturated acid which decomposes at 160°.
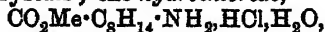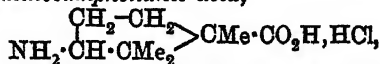
E. G.

New Methods of Preparation of Camphonenic (γ-Lauronolic) Acid and the Relation of the Latter to Laurolenic (Lauronolic) Acid. JULIUS BREDT [and, in part, PAUL LEVY and S. LINK] (*J. pr. Chem.*, 1913, [ii], 87, 1—11).—The first part of this paper is mainly a summary of the authors' views on the constitution and relationships of the lauronolic acids and allied compounds, together with suggestions concerning their nomenclature (compare A., 1911, i, 417).

When submitted to slow distillation, dehydrocamphoric acid (A., 1902, i, 374) loses carbon dioxide, yielding γ-lauronolic (camphonenic) acid (I). It is accompanied by *iso*dehydrocamphoric anhydride, from which it may be separated by distillation in steam. When purified by the calcium salt, $C_{18}H_{26}O_4Ca,H_2O$, and repeatedly crystallised from dilute acetic acid it is obtained in feather-like crystals, m. p. 155—156° (compare Noyes, A., 1912, i, 159).

Dehydrocamphoric acid combines with hydrobromic acid, yielding a mixture of two stereoisomeric *hydrobromides* (II), of which the *cis*-form has m. p. 168—170°, and is reduced by zinc and acetic acid to *cis*-camphoric acid, whilst the *cis-trans*-modification has m. p. 232°, and on reduction yields *cis-trans*-camphoric acid :

$$CH{=}C{\cdot}CO_2H \qquad CHBr{\cdot}CH{\cdot}CO_2H \qquad CH(OH){\cdot}CH$$
$$\overset{|}{C}Me_2 \qquad\qquad \overset{|}{C}Me_2 \qquad\qquad\quad \overset{|}{C}Me_2$$
$$\overset{|}{C}H_2{\cdot}CMe{\cdot}CO_2H \quad \overset{|}{C}H_2{-}\overset{|}{C}Me{\cdot}CO_2H \quad \overset{|}{C}H_2{-}\overset{|}{-}CMe{\cdot}CO_2H$$
$$\text{(I.)} \qquad\qquad\qquad \text{(II.)} \qquad\qquad\qquad \text{(III.)}$$
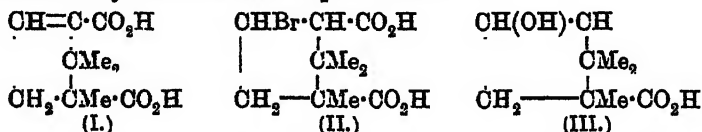
When boiled in aqueous solution the sodium salt of the *cis-trans*-hydrobromide yields as main product a *hydroxy-acid* (III), which is accompanied by γ-lauronolic acid (10%).

Oxidation of γ-lauronolic acid with nitric acid, or of its calcium salt with potassium permanganate, gives rise to camphoronic acid.   F. B.

A New Method of Preparation of Laurolenic (Lauronolic) Acid and the Decomposition of Camphanic Acid in an Electric Reflux Heater under Diminished Pressure. JULIUS BREDT and AUGUST AMANN (*J. pr. Chem.*, 1913, [ii], 87, 12—26).—Lauronolic acid, which the authors now terms laurolenic acid, is obtained by boiling γ-camphonanic acid (A., 1912, i, 113) for a short time with aqueous sodium carbonate. It is accompanied by camphonololactone, and has also been prepared (1) by distillation of camphanic acid under diminished pressure in a specially constructed, electrically heated apparatus, a sketch of which is given, and (2) by heating chlorocamphoric anhydride (A., 1912, i, 411) with aqueous sodium carbonate. The m. p. of the acid varies from 5·5—7° to 8·5—10° according to its method of preparation, and $[a]_D$ from 181·3° to 195·2°.

The calcium salt separates from its aqueous solution at the ordinary temperature with $2H_2O$, and not $3H_2O$, as stated by Noyes and Burke (A., 1912, i, 159).   F. B.

Methods for the Preparation of Neutral Solutions of Ammonium Citrate. JAMES M. BELL and CHARLES F. COWELL (*J. Amer. Chem. Soc.*, 1913, 35, 49—54).—The methods at present

employed for the preparation of neutral solutions of ammonium citrate are not satisfactory and two new methods have therefore been devised. In one of these methods, the excess of ammonia is estimated by extracting the solution with chloroform, and titrating the chloroform with 0·1N-hydrochloric acid in presence of methyl-red as indicator. In the other method, the rise of temperature due to the heat of neutralisation is observed as the citric acid solution is titrated with ammonia, the end-point being at the break in the heating curve. Both these methods are considered to be simpler than that involving the determination of the conductivity of solutions at constant temperature.

E. G.

Thio-γ-valerolactone. KARL FRIES and H. MENGEL (*Ber.*, 1912, 45, 3408—3411).—On heating valerolactone with phosphorus pentasulphide, *thio-γ-valerolactone*, $CHMe{<}^{CH_2 \cdot CH_2}_{S\ ---\ CO}$, is obtained as a colourless oil of pleasant aromatic odour, b. p. 94—95°/20 mm. It is readily hydrolysed by alkali hydroxides to γ-mercaptovaleric acid, which is reconverted into the thiolactone on treatment with mineral acids.

A further product of the action of the pentasulphide is *dithio-γ-valerolactone*, $CHMe{<}^{CH_2 \cdot CH_2}_{S\ ---\ CS}$, an orange-coloured, viscid oil of unpleasant odour. Condensing agents such as sodium methoxide convert it very readily into *trithio-di-γ-valerolactone*,

$$CHMe{<}^{CH_2 \cdot CH_2}_{S\ ---\ C}\ \ {}^{CS \cdot S}_{C \cdot CH_2}{>}CHMe,$$
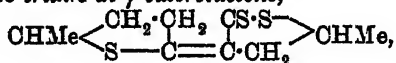
which crystallises in bunches of large, red prisms, m. p. 77°.

E. F. A.

Maleindialdehyde. ALFRED WOHL and BRUNO MYLO (*Ber.*, 1912, 45, 1746—1756).—Maleindialdehyde diethylacetal, an intermediate product in the preparation of tartardialdehyde (A., 1912, i, 162), has been hydrolysed by means of dilute sulphuric acid, and the maleindialdehyde has been characterised. The most striking property of this compound is its yellow colour, which is more intense than that of diacetyl and may be accounted for by the grouping together of conjugated double bonds and the conveying of the influence of one carbonyl group to the other by an ethylenic linking. Oxidation by silver carbonate gives maleic and also fumaric acids, and since the original acetal yields a tartardialdehyde acetal of the type of mesotartaric acid (*ibid.*), it is suggested that this is the real maleindialdehyde, whereas that obtained by Marquis from nitrosuccinaldehyde monoacetin (A., 1905, i, 224) is fumardialdehyde, especially as the nitrous acid which is formed at the same time has a great tendency to convert maleic into fumaric acid.

For the preparation of *maleinlialdehyde*, $CHO \cdot CH{:}CH \cdot CHO$, 35 grams of the acetal are shaken with 150 c.c. of $N/10$-sulphuric acid and the faintly yellow, pungent smelling solution is exactly neutralised with barium hydroxide. After removing the barium sulphate by centrifugation, the solution is evaporated at 40° in a vacuum with a

fractionating column which, however, does not prevent the loss of some aldehyde, since it is volatile in steam, and the residue is extracted with chloroform and dried. The extract is evaporated in the same way and the syrupy residue is maintained at 105—115°/9 mm., when the polymeric substances slowly decompose and the aldehyde distils over. The distillate is collected in a Claisen flask in a freezing mixture and redistilled from a bath already heated to 75°, when the mobile, yellow, pungent-smelling aldehyde boils at 56—59°/9·5 mm. It dissolves in water and organic solvents, and probably forms hydrates and alcoholates, since yellow aqueous or alcoholic solutions soon become colourless. It is only slowly affected by oxygen or bromine water, but it immediately reduces permanganate or ammoniacal silver oxide. At the ordinary temperature it very quickly changes to a syrup with less intense colour and odour, and it is then only slightly soluble in ether, benzene or warm water. From the aqueous solution an amorphous solid separates out ; probably a syrupy and a solid polymeride exist.

Derivatives of the dialdehyde have been prepared by hydrolysing the acetal, exactly neutralising with sodium carbonate, and precipitating with the free base in the cold. The *diphenylhydrazone*, NHPh·N:CH·CH:CH·CH:N·NHPh, forms unstable, yellow, quadratic leaflets from hot alcohol, m. p. 198—199°; Marquis's dihydrazone melts at 236—237° (*ibid.*). It gives a reddish-violet compound on oxidation, which is similar to, but not identical with, Marquis's "tetrazone" ; they are probably not tetrazones at all. The *dioxime*, $C_4H_6O_2N_2$, forms pure white needles from hot methyl alcohol which decompose with violence at 150—155°; Marquis's compound decomposes at 220° (*ibid.*). The *disemicarbazone*, $C_6H_{10}O_2N_6$, is only very slightly soluble, and crystallises best from a large volume of boiling water in slender needles, m. p. 246—247° (corr.).   J. C. W.

The Isomeric Changes of Dextrose Produced by Alkalis. Theory of Catalytic Action. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1912, **47**, 447—461).—The changes in dextrose (measured chiefly polarimetrically) produced by alkalis (in presence of phosphates, etc., added to keep the hydrogen-ion concentration constant during the experiment) is directly proportional to the hydroxyl-ion concentration. The acid nature of dextrose was demonstrated, and its dissociation constant was found to be $5 \cdot 10^{-13}$. This was measured by ascertaining the changes in the hydroxyl-ion concentration of sodium hydroxide solutions (measured electrometrically) produced by the addition of dextrose. From these facts, the hypothesis is put forward, that the "catalytic" action of the hydroxyl ions increases the number of sugar ions, according to theory of mass action, and it is the latter which spontaneously undergo isomeric change.   S. B. S.

Conversion of *d*-Glucose [Dextrose] into a Methylpentose. EMIL FISCHER and KARL ZACH (*Ber.*, 1912, **45**, 3761—3773).— Triacetylmethylglucoside bromohydrin (Fischer and Armstrong, A., 1902, i, 263), $CH_2Br·CH(OAc)·OH·CH(OAc)·CH(OAc)·CH(OMe)$
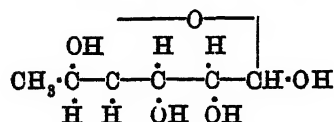
is converted on reduction with acetic acid and zinc dust into a tri-acetyl derivative which on alkaline hydrolysis yields *β-methyl*-d-*iso*-*rhamnoside*, $CH_3 \cdot CH(OH) \cdot CH \cdot CH(OH) \cdot CH(OH) \cdot CH \cdot OMe$. This is

$$CH_3 \cdot \overset{H}{\underset{\overset{|}{OH}}{\overset{|}{C}}} - \overset{H}{\underset{'}{\overset{|}{C}}} - \overset{OH}{\underset{\overset{|}{H}}{\overset{|}{C}}} - \overset{H}{\underset{\overset{|}{OH}}{\overset{|}{C}}} - CH \cdot OH$$

hydrolyed by acids to *d-iso*rhamnose (annexed formula), which is identical with the *iso*rhodeose described by Votoček (A., 1911, i, 354), and obtained by him from purgic acid. Since no asymmetric carbon atom is concerned in the series of reactions, no Walden rearrangement is possible, and the methylpentose has the same configuration as *d*-glucose.

Accordingly the annexed formula of *l*-rhamnose (methyl-*l*-mannose), which was hitherto uncertain, is established.

$$CH_3 \cdot \overset{OH}{\underset{\overset{|}{H}}{\overset{|}{C}}} - \overset{H}{\underset{\overset{|}{H}}{\overset{|}{C}}} - \overset{H}{\underset{\overset{|}{OH}}{\overset{|}{C}}} - \overset{}{\underset{\overset{|}{OH}}{\overset{|}{C}}} - CH \cdot OH$$

β-Methyl-*d-iso*rhamnoside, like *β*-methylglucoside, is hydrolysed by emulsin, whereas *β*-methylxyloside is not attacked. Renewed emphasis is laid on this remarkable difference in view of the similarity in structure of ·the three glucosides.

Triacetyl-methyl-d-*iso*rhamnoside crystallises in well-formed, colour-less needles, m. p. 100° (corr.), $[a]_D^{20} - 20 \cdot 22°$.

β-Methyl-d-*iso*rhamnoside forms slender, colourless needles, m. p. 133° (corr.), $[a]_D^{20} - 55 \cdot 3°$, which taste bitter.

*d-iso*Rhamnose separates in hard, colourless crystals in a variety of forms, m. p. 139—140° (corr.). The rotation changes from $[a]_D^{20} + 73 \cdot 3°$ to $+ 29 \cdot 7°$ in aqueous solution.

*d-iso*Rhamnosephenylosazone crystallises in yellow needles, m. p. 185° (corr.), to a dark red liquid (compare Votoček, *loc. cit.*), $[a]_D^{20} - 95°$ in white light; it is the optical antipode of *l*-rhamnosephenyl-osazone.

*d-iso*Rhamnonolactone has m. p. 151—152° (corr.), $[a]_D^{20}$ changing from $+ 66 \cdot 88°$ to $+ 5 \cdot 35°$.   E. F. A.

Properties of Phytin. M. A. EGOROV (*Bied. Zentr.*, 1912, 42, 66—67 ; from *J. Exper. Landw.*, 1912, 12, 361).—The phosphoric acid of phytin, which is precipitated by acid molybdate solution, is not pre-cipitated under ordinary conditions in ammonium citrate solution by magnesia mixture.

When phytin is boiled with water for fourteen to sixteen hours it is completely decomposed with production of inositol and inorganic phosphoric acid compounds. The yield of phosphoric acid is about 100%.   N. H. J. M.

Formation of Humus and Combustible Minerals without the Intervention of Atmospheric Oxygen, Micro-organisms, High Temperatures, or Great Pressure. LOUIS C. MAILLARD (*Compt. rend.*, 1912, 155, 1554—1556).—A theoretical discussion of work previously described (compare A., 1912, i, 13, 169). The author has now shown that oxidation does not intervene in any way in

the generation of carbon dioxide and the production of humic substances by the interaction of sugars and amino-acids. He has further obtained a jet black substance, rich in carbon and containing nitrogen, which exhibits a remarkable resistance to reagents, and he suggests that this reaction should be taken into account in framing theories as to the formation of combustible minerals.   W. G.

Some Unstable Nitrites Fixed by means of Organic Bases. III. GINO SCAGLIARINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 640—643).—The author describes stable compounds of the nitrites of mercury, zinc, and cadmium with hexamethylenetetramine. The substances were prepared by adding sodium nitrite to a solution of a salt of the metal in the presence of hexamethylenetetramine. The *compound*, $2Hg(NO_2)_2,8H_2O,3C_6H_{12}N_4$, forms white crystals with a greenish lustre. The *compound*, $Zn(NO_2)_2,2H_2O,C_6H_{12}N_4$, forms colourless prismatic crystals, as does also the *compound*,

$$Cd(NO_2)_2,2H_2O,C_6H_{12}N_4.$$ R. V. S.

Alloxan Anhydride and Its Methyl Derivatives. HEINRICH BILTZ (*Ber.*, 1912, 45, 3659—3675).—By heating under reduced pressure it is found possible completely to dehydrate alloxan and its methyl and dimethyl derivatives ; the anhydrous substances have an intense yellow colour and can be sublimed unchanged in a vacuum.

Alloxan anhydride, $C_4H_2O_4N_2$, obtained by heating the monohydrate for an hour at 210—220° in a vacuum produced by a mercury pump, forms yellow, rhombic crystals ($a:b:c=0.9974:1:1.6841$), m. p. 256° (decomp.). A partial dehydration of the monohydrate is also effected by recrystallising from acetic acid.

Methylalloxan anhydride, obtained from the monohydrate by similar treatment to the previous but at 160°, separates from acetic acid in leafy crystals (rhombic system, $a:b:c=0.6766:1:?$), m. p. 154—156° (decomp.).

Dimethylalloxan anhydride (compare Holleman, A., 1897, i, 599) could be obtained from the monohydrate by heating in a water-pump vacuum at 210—220°; it crystallises from benzyl cyanide in short, yellow columns (rhombic system, $a:b:c=0.6847:1:?$).

[With E. TOPP.]—The above anhydrous compounds separated from alcohols containing a little hydrogen chloride in the form of alcoholates which are analogous to the phenolates described earlier (Boehringer & Söhne, D.R.P. 1898, 107720; 1899, 113722). *Alloxan ethyl alcoholate*, $CO\!<\!{{NH-CO}\atop{NH-CO}}\!>\!C(OH)\cdot OEt$, prisms; *alloxan methyl alcoholate*, prisms; *alloxan benzyl alcoholate*, prisms.

Methylalloxan ethyl alcoholate, tablets.

*Dimethylalloxan ethyl alcoholate*, tetragonal prisms, m. p. 95°; *dimethylalloxan methyl alcoholate*, m. p. circa 90°, hexagonal tablets; *dimethylalloxan benzyl alcoholate*, crystals, m. p. 185—188°.

All these alcoholates when heated eliminate the molecule of alcohol, giving a residue which has approximately the m. p. of the pure anhydride.

The following compounds were prepared by crystallisation from a

solution of the anhydride and a phenol with hydrogen chloride in acetic acid ; *alloxan phenolate*, decomposing at 240—245°; alloxan *p*-cresolate decomposing at 228—230° (compare Boehringer & Söhne, *loc. c.t.*); *dimethylalloxan* p-*cresolate*, hexagonal prisms, m. p. 105°.

[With J. KARTTE.]—An aqueous solution of dimethylalloxan dihydrate when saturated with sulphur dioxide and evaporated in a vacuum desiccator deposits *dimethylalloxan sulphite*,

$$CO<^{NMe\cdot CO}_{NMe\cdot CO}>C(OH)\cdot SO_3\cdot C(OH)<^{CO\cdot NMe}_{CO\cdot NMe}>CO,$$
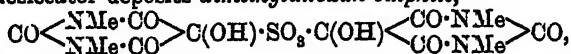
colourless prisms, which decompose at 75°. *Methylalloxan sulphite*, obtained in an analogous manner, crystallises in prisms with $4H_2O$. *Alloxan sulphite* forms rhombic leaflets, decomposing near 184°.

Alloxan anhydride condenses in alcoholic acetic acid solution with dimethylcarbamide producing 7 : 9-dimethyluric acid glycol (compare Biltz and Krebs, A., 1910, i, 526), but the product from dimethylalloxan anhydride and dimethylcarbamide was allocaffeine (compare Biltz and Krebs, *loc. cit.*, i, 521).

Working details are given of the methods found most suitable for the preparation of di- and tetra-methylalloxantin and their conversion into methyl- and dimethyl-alloxans.   D. F. T.

The System Ammonium Thiocyanate–Thiocarbamide–Water. ANDREAS SMITS and A. KETTNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 683—686).—The investigation of the melting-point diagram of the pseudo-binary system ammonium thiocyanate–thiocarbamide has given results which indicate the existence of a compound $NH_4CNS,4CS(NH_2)_2$, whereas Atkins and Werner (T., 1912, 101, 1167) are of the opinion that the compound has the composition $NH_4CNS,3CS(NH_2)_2$. The evidence for the former is supported by the results of the determination of the solubility isotherms at 25° and the examination of the co-existing solid phases by the residue method. The solubility curves afford a simple explanation of the method of preparation of thiocarbamide from ammonium thiocyanate recommended by Reynolds and Werner (T., 1903, 83, 1), which up to the present has not been satisfactorily accounted for.   H. M. D.

Selective Catalysis of Dehydrogenation. NICOLAI D. ZELINSKI (*Ber.*, 1912, 45, 3678—3682).—The catalytic dehydrogenation of *cyclo*hexane compounds by palladium or platinum at 300° and the inactivity of these metals towards *cyclo*pentane compounds under the same conditions can be applied to the separation of *cyclo*hexane and *cyclo*pentane hydrocarbons.

[With (Frl.) A. HERZENSTEIN.]—After a mixture of equal volumes of methyl*cyclo*pentane and *cyclo*hexane has been thrice submitted to the action of platinum black at 300°, no further liberation of hydrogen occurs, and the hydrogen collected amounts to more than 90% of the theoretical. After removal of the benzene from the resultant hydrocarbon mixture by treatment at the ordinary temperature with sulphuric acid (two volumes of acid, D 1·84, mixed with one volume of fuming acid containing 7% of anhydride), the residual liquid was pure methyl*cyclo*pentane.

*cyclo*Heptane resembles *cyclo*pentane (Zelinski, A., 1911, i, 958) in resisting the above catalytic dehydrogenation.

A specimen of naphtha, b. p. 102—104°, D^{18} 0·7647, n^{18} 1·4215, from Baku petroleum, by the above treatment gave a liquid which could be separated by distillation into two fractions. The less volatile fraction, b. p. 105—107°, contained much toluene, whilst the other fraction, b. p. 104—105°, after one more treatment with platinum black followed by the removal of any aromatic hydrocarbons by means of the special sulphuric acid mentioned above, gave a hydrocarbon, C_7H_{14}, b. p. 101—102·5°/747 mm., D_4^{20} 0·7488, n^{20} 1·4101, which is probably a *cyclo*pentane or *cyclo*butane derivative.

[With W. DOBROCHOTOV.]—Another specimen of naphtha, b. p. 100—100·5°, D^{18} 0·766, $n^{20\cdot5}$ 1·4210, when submitted to the action of platinum black at 300°, liberated much hydrogen, and after the removal of toluene and redistillation had b. p. 100—101°, D_4^{18} 0·7490, n^{18} 1·4142. The original hydrocarbon, a "heptanaphthene," which had been previously treated with a mixture of nitric and sulphuric acids, had therefore yielded a *cyclo*paraffin product very similar to that obtained from the above naphtha fraction (b. p. 102—104°), which had not been first treated with nitric and sulphuric acids.   D. F. T.

Formation of Dimethylstyrene [β-Phenyl-Δ^β-butylene] from Phenyldimethylethyl Alcohol [β-Phenyl*iso*butyl Alcohol]. ALBIN HALLER and ÉDOUARD BAUER (*Compt. rend.*, 1912, 155, 1581—1585).—By the action of sodamide on phenylacetonitrile (1 mol.) in ethereal solution followed by the addition of methyl iodide (1 mol.), a liquid, b. p. 115—120°/19—20 mm., is obtained, which on further treatment with sodamide and methyl iodide gives α-phenyl*iso*butyronitrile (compare Wallach, A., 1900, i, 229). This substance on hydrolysis with 85% sulphuric acid on a water-bath furnishes the corresponding amide, which by reduction with sodium in absolute alcohol yields *β-phenyliso*butyl alcohol, $CPhMe_2·CH_2·OH$, b. p. 122—123°/20 mm., which gives a *phenylurethane*, white needles, m. p. 59—60°. During the reduction there is produced at the same time some β-phenyl*iso*butylamine, b. p. 115—116°/20 mm. (compare Wallach, *loc. cit.*), which forms a *platinichloride*, insoluble in water.

By acting on β-phenyl*iso*butyl alcohol with thionyl chloride in slight excess at 0°, a liquid is obtained separable into two fractions, of which one is β-phenyl·Δ^β-butylene, $CPhMe{:}CHMe$ (compare Klages, A., 1902, i, 666; 1903, i, 19), and the other a *chloride*, $C_{10}H_{13}Cl$, b. p. 104—105°/20 mm., the constitution of which has not yet been established. With silver acetate, it gives an *acetate*, which on saponification gives an *alcohol*, b. p., 115—117°/15 mm., isomeric with the alcohol from which the chloride was derived.   W. G.

2 : 4 : 6-Tribromo-1-iodo-3-nitrobenzene. C. LORING JACKSON and WEBSTER N. JONES (*Amer. Chem. J.*, 1913, 49, 46—55).—2 : 4 : 6-Tribromo-3-nitroaniline (Körner, A., 1876, i, 210) has m. p. 101·5°. Remmers (A., 1874, 696) assigned the m. p. 214—215° to this compound, but it is now shown that his substance was probably 2 : 4 : 6-tribromo-3-nitroacetanilide.   2 : 4 : 6 - Tribromo - 3 - nitrodiacetanilide

(Remmers, *loc. cit.*) has m. p. 168—169°, and seems to be identical with the substance supposed by Wheeler (A., 1896, i, 157) to be the monoacetanilide. 2 : 4 : 6-*Tribromo-3-nitroacetanilide*, m. p. 208—209°, forms white, rhombic crystals.

2 : 4 : 6-*Tribromo-1-iodo-3-nitrobenzene*, $C_6HBr_3I \cdot NO_2$, m.p. 144—145°, obtained by the action of potassium iodide on the diazotisation product of 2 : 4 : 6-tribromo-3-nitroaniline, crystallises in white, rectangular plates. When this substance is treated with a solution of sodium ethoxide, it is converted into a *dibromoiodonitrophenetole*,

$$NO_2 \cdot C_6HBr_2I \cdot OEt,$$
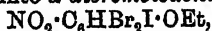
m. p. 121°, which forms long, white, rectangular prisms; other compounds are produced in this reaction, one of which has m. p. 149°.

E. G.

The Nitration of the Chlorotoluenes. ARNOLD F. HOLLEMAN and J. P. WIBAUT (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 594—599).—The position assumed by a third substituent in a benzene ring depends on the relative velocities of substitution caused by the two substituents already present. The hydroxyl, amino-, halogen and methyl groups which cause ortho-para substitution are placed in the order of decreasing velocity.

In order to obtain further knowledge of the relative substitution velocity caused by different groups, the author has re-investigated the nitration products of *o*-chlorotoluene (Goldschmidt and Hönig, A., 1886, 1022). All four possible chloronitrotoluenes, 2 : 3, 2 : 4, 2 : 5, 2 : 6, were found to be present in the product, although the 2 : 4-isomeride proved difficult of detection. For the estimation of the relative amounts of the isomerides in the nitration product, Valeton's modification of the m.-p. method was used, and indicated in a product obtained at 0° from 10 grams of chlorotoluene and 40 grams of nitric acid (D 1·52), 19·2, 17·0, 43·3, and 20·5% respectively, in the above order.

In extending a similar investigation to the nitration of *m*-chlorotoluene, 3 : 6-, 3 : 5-, 3 : 4-, and 3 : 2-chloronitrotoluenes were prepared in a high state of purity, and had m. p. 24·9°, 58·4°, 24·2°, and 23·4° respectively. Analysis of the reaction product indicated no appreciable quantity of the 3 : 5-isomeride, and 58·9, 32·3, and 8·8% of the remaining three.

By a calculation involving the composition of the nitration products of toluene, chlorobenzene and *p*-chlorotoluene, it is deduced that chlorine causes a velocity of substitution 1·491 times as great as that caused by the methyl radicle. The knowledge of this number allows the calculation of the proportion in which the various isomeric products should be formed in the nitration of *o*- and *m*-chlorotoluenes, and the theoretical proportions exhibit a gratifying concordance with the experimental. D. F. T.

αα Dihalogenoarylsulphonylacetonitriles, $R \cdot SO_2 \cdot CX_2 \cdot CN$, and a Peculiar Reduction of these Halogen Compounds. JULIUS TRÖGER and W. KROSEBERG (*J. pr. Chem.*, 1913, [ii], 87, 67—84. Compare A., 1905, i, 336, 870; 1908, i, 633, 798).—It has been shown previously that αα-dibromoarylsulphonylacetonitriles may be

obtained readily by the action of bromine on the sodium salts of arylsulphonyl-α-oximinoacetonitriles, $SO_2R \cdot C(:NOH) \cdot CN$, in aqueous solution. Attempts to prepare the corresponding dichloro- and di-iodo-compounds in a similar manner were unsuccessful. The dichloro-compounds may, however, be obtained by the addition of bleaching powder to a glacial acetic acid solution of the corresponding arylsulphonylacetonitriles, $SO_2R \cdot CH_2 \cdot CN$.

The following compounds were prepared in this manner: *aa-dichlorobenzenesulphonylacetonitrile*, $SO_2Ph \cdot CCl_2 \cdot CN$, lustrous prisms, m. p. 57°; *aa-p-trichlorobenzenesulphonylacetonitrile*, white needles, m. p. 96—97°; *aa-dichloro-p-bromobenzenesulphonylacetonitrile*, stout needles, m. p. 105—106°; *aa-dichloro-p-iodobenzenesulphonylacetonitrile*, flat prisms, m. p. 111—112°; *aa-dichloro-p-toluenesulphonylacetonitrile*, broad, lustrous needles, m. p. 92°; *aa-dichloro-p-methoxybenzenesulphonylacetonitrile*, m. p. 121°; *aa-dichloro-p-ethoxybenzenesulphonylacetonitrile*, m. p. 95°; *aa-dichloro-ψ-cumenesulphonylacetonitrile*, m. p. 103—104°, and *aa-dichloro-a-naphthalenesulphonylacetonitrile*, m. p. 118°.

The benzenesulphonyl derivative may also be prepared by directly chlorinating benzenesulphonylacetonitrile in glacial acetic acid solution. When dissolved in aqueous sodium hydroxide and the solution treated with a large excess of sodium hypochlorite, benzenesulphonylacetonitrile yields phenyl dichloromethyl sulphone, $CHCl_2 \cdot SO_2Ph$.

aa-Dibromo-p-toluenesulphonylacetonitrile, prepared from *p*-toluenesulphonylacetonitrile and bromine in glacial acetic acid solution, crystallises in long, white prisms, m. p. 121°; *aa-dibromo-o-methoxybenzenesulphonylacetonitrile* forms small prisms, m. p. 123°; *aa-dibromo-p-ethoxybenzenesulphonylacetonitrile*, stout, white needles, m. p. 118°; *aa-dibromo-ψ-cumenesulphonylacetonitrile* crystallises in prisms, m. p. 123°; *aa-dibromo-a-naphthalenesulphonylacetonitrile*, in pale yellow needles, m. p. 146°.

Attempts have been made to prepare compounds of the type $SO_2R \cdot CO \cdot CN$: (1) by hydrolysing the α-oximinoarylsulphonylacetonitriles with dilute acids; (2) by the action of silver oxide on the above dihalogen compounds, and (3) by oxidising the arylsulphonylacetonitriles with potassium permanganate, but so far these attempts have not met with success.

When heated with sodium benzenesulphinate in alcoholic solution, *aa*-dihalogenoarylsulphonylacetonitriles undergo a remarkable reduction to arylsulphonylacetonitriles, thus: $SO_2R \cdot CX_2 \cdot CN + 2SO_2PhNa + 2H_2O = 2NaX + 2SO_2Ph \cdot OH + SO_2R \cdot CH_2 \cdot CN$.

The action of iodine dissolved in aqueous potassium iodide on the sodium salt of α-oximinobenzenesulphonylacetonitrile leads to the formation of the corresponding *potassium* salt, $SO_2Ph \cdot C(CN):NOK$, which crystallises in lustrous, golden-yellow leaflets.

The authors also record unsuccessful attempts to prepare compounds of the type $SO_2R \cdot C(CN):NO \cdot ONa$ by the condensation of ethyl nitrate and arylsulphonylacetonitriles by means of sodium ethoxide in alcoholic solution; in the case of *p*-chlorobenzenesulphonylacetonitrile, the product of the reaction consisted of the *sodium* salt,

$$C_6H_4Cl \cdot SO_2 \cdot CHNa \cdot CN.$$
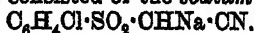
F. B.

Spontaneous Formation of Iodonium Bases Containing Iodine in a Pentatomic Heterocyclic Nucleus. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 61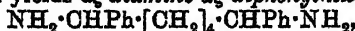7—620).—When 2 : 2'-di-iodosodiphenyl, $IO \cdot C_6H_4 \cdot C_6H_4 \cdot IO$, or 2:2'-di-iododiphenyl tetrachloride, $ICl_2 \cdot C_6H_4 \cdot C_6H_4 \cdot ICl_2$, are kept in water for some months, the aqueous solution yields diphenyleneiodonium iodide, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > I \cdot I$, when treated with sulphur dioxide. In the case of the tetrachloride, the di-iodoso-derivative is probably first formed, together with hydrogen chloride. By subsequent simultaneous oxidation and reduction of the di-iodoso-compound, all the following substances may be produced : $C_6H_4I \cdot C_6H_4I$, $IO_2 \cdot C_6H_4 \cdot C_6H_4 \cdot IO_2$, $C_6H_4I \cdot C_6H_4 \cdot IO_2$, $IO \cdot C_6H_4 \cdot C_6H_4 \cdot IO_2$, and $C_6H_4I \cdot C_6H_4 \cdot IO$. By rearrangement of the compound
$$IO \cdot C_6H_4 \cdot C_6H_4 \cdot IO_2,$$
diphenyleneiodonium iodate, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} > I \cdot IO_3$, is produced, and this, by the action of sulphur dioxide, is reduced to the iodide (compare Forster and Schaeppi, T., 1912, 101, 1359).   R. V. S.
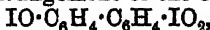
ωω'-Diarylated Aliphatic Hydrocarbons. WALTHER BORSCHE and J. WOLLEMANN (*Ber.*, 1912, 45, 3713—3725. Compare A., 1912, i, 23).—The method for the synthesis of αK-diphenyldecane has now been extended to the preparation of other members of the series, with certain modifications in the case of the pentane, heptane, and nonane.
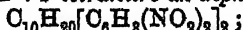
Adipyl chloride, from adipic acid and phosphorus trichloride, condenses with benzene to form αζ-diphenylhexan-αζ-dione, m. p. 107° (Etaix, A., 1898, i, 124), δ-*benzoylvaleric acid*, $COPh \cdot [CH_2]_4 \cdot CO_2H$, being formed at the same time in white needles, m. p. 70—72°. The diketone has been converted into the dioxime, m. p. 222—223° (*ibid.*), which on reduction yields αζ-*diamino-αζ-diphenylhexane*,
$$NH_2 \cdot CHPh \cdot [CH_2]_4 \cdot CHPh \cdot NH_2,$$
as a colourless oil, b. p. 250—254°/16 mm., the *carbamide* of which, $C_{20}H_{26}O_2N_4$, melts at 121°, and the *benzoyl* derivative, $C_{32}H_{32}O_2N_2$, at 238°. The conversion of the diamine into Rupe and Bürgin's αζ-diphenyl-Δ$^{α-}$hexadiene (A., 1910, i, 161) gives a poor result, but the method of von Braun and Deutsch (A., 1912, i, 687) provides a better way of obtaining the desired αζ-diphenylhexane.

In the same way, suberyl chloride has been converted into the corresponding dioxime (Etaix, *loc. cit.*), and this has been reduced and the phosphate of the diamine has been distilled. A good yield of αθ-*diphenyl-Δ^{αη}-octadiene*, $CHPh:CH \cdot [CH_2]_4 \cdot CH:CHPh$, is thus obtained in colourless leaflets, m. p. 61—62°, b. p. 210—220°/11 mm. ; it gives a *tetrabromide*, $C_{20}H_{22}Br_4$, m. p. 196°, and absorbs hydrogen in the presence of palladium, yielding αθ-diphenyloctane (compare Braun and Deutsch, *loc. cit.*).

A characteristic derivative of αK-diphenyldecane (*loc. cit.*) is the nitration product, 2 : 4 : 2' : 4'-*tetranitro-αK-diphenyldecane*,
$$C_{10}H_{20}[C_6H_3(NO_2)_2]_2 ;$$
it forms yellowish-white needles, m. p. 63°.

The acid chlorides for the corresponding pentane, heptane, and nonane are difficult to obtain, and the diamines would probably yield ring compounds. Hence, the necessary ketones have been prepared by the reduction of available unsaturated ketones (compare A., 1912, i, 194) and reduced to alcohols, which, on dehydration with zinc chloride, give the olefines. The reduction of distyryl ketone to di-β-phenylethyl ketone is usually accompanied by by-products, the nature of which seems to depend on the condition of the palladium employed. The substance, $C_{34}H_{34}O_2$, m. p. 126° (*ibid.*), has not since been encountered ; instead, the $\alpha\epsilon\zeta\kappa$-tetraphenyldecane-$\theta$-dione, $C_{34}H_{34}O_2$, m. p. 173—174°, of Harries and Gollnitz (A., 1904, i, 427), and, apparently, its unsaturated *ketone*, $C_{34}H_{30}O_2$, a white powder, m. p. 207—208°, which dissolves with a purple colour in concentrated sulphuric acid, have been isolated. The required di-β phenylethyl ketone can be more conveniently prepared from phenylethyl methyl ketone by saturating its benzylidene compound (Harries and Gollnitz, *loc. cit.*) with hydrogen in presence of palladium. On reduction with sodium and alcohol, $\alpha\epsilon$-*diphenylpentan-γ-ol*, $OH \cdot CH(CH_2 \cdot CH_2Ph)_2$, is obtained as a very soluble, crystalline mass, m. p. 47—48°, b. p. 218°/11 mm., which, on distillation with zinc chloride, yields $\alpha\epsilon$-*diphenyl Δ^β-pentene* as a colourless oil, b. p. 184—185°/10 mm. Reduction readily results in the $\alpha\epsilon$ diphenylpentane of Braun and Deutsch (A., 1912, i, 435). The same series of reactions has also been carried out with phenyl δ-phenylbutyl ketone (A., 1912, i, 194), which has been obtained in colourless needles, m. p. 47°. $\alpha\epsilon$-*Diphenylpentan-α-ol*, $OH \cdot CHPh \cdot [CH_2]_3 \cdot CH_2Ph$, is a colourless oil, b. p. 217°/12 mm., which gives a poor yield of $\alpha\epsilon$-*diphenyl-Δ^α-pentene*, a colourless, mobile liquid, b. p. 186°/11 mm., which polymerises when heated. The $\alpha\epsilon$-diphenylpentane forms a *tetranitro*-derivative, $C_{17}H_{16}O_8N_4$, in slender, yellow needles, m. p. 126°.

$\alpha\eta$-Diphenylheptan-γ-one is best obtained by the reduction of $\alpha\eta$-*diphenyl-Δ^α-hepten-γ-one*, $CHPh \cdot CH \cdot CO \cdot [CH_2]_3 \cdot CH_2Ph$, which is formed in colourless leaflets, m. p 25°, b. p. 240°/12 mm., by the condensation of benzaldehyde with methyl-δ-phenylbutyl ketone (A., 1911, i, 880). Its reduction product, $\alpha\eta$-*diphenylheptan-γ-ol*, m. p. 42—43°, b. p. 233°/11 mm., is very readily dehydrated, and the heptene is also easily reduced to $\alpha\eta$ diphenylheptane, b. p. 207—208°/12 mm.

In the same way, $\alpha\iota$-diphenylnonan-ϵ-one (A., 1912, i, 194) has been reduced to $\alpha\iota$-*diphenylnonan-ϵ-ol*, a viscous, colourless liquid, b. p. 251°/11 mm., which yields the $\alpha\iota$-*diphenyl-Δ^δ-nonene* as a highly refractive oil, b. p. 231—233°/12 mm. Reduction of the latter to $\alpha\iota$-*diphenylnonane*, a colourless oil, b. p. 235°/12 mm., proceeds very readily.   J. C. W.

Pyrosulphates of Sodium and Potassium as Condensing Agents. ALLAN F. ODELL and CLEVE W. HINES (*J. Amer. Chem. Soc.*, 1913, 35, 81—84).—The alkali pyrosulphates have been used as condensing agents by Bogojavlenski and Narbutt (A., 1905, i, 854) in the preparation of certain esters. The salts are readily converted into the hydrogen sulphates by the addition of water, and should,

therefore, be efficient agents for the abstraction of water in organic synthesis ; they are easily prepared and convenient to handle.

The pyrosulphates have now been applied to the preparation of triphenylbenzene, benzylideneaniline, benzylidenemalonic acid, phenylstyryl ketone and acetanilide, and have given good results. They cannot be employed, however, to effect the condensation of phenols with other substances.   E. G.

Nitro-derivatives of *m*-Cresyl Oxide [*m*-Tolyl Ether]. ALPHONSE MAILHE (*Compt. rend.*, 1912, 155, 1524—1526).—A study of the nitration of *m*-tolyl ether prepared by the aid of thorium oxide (compare A., 1912, i, 767). Nitration in acetic acid solution at the ordinary temperature yields *nitro-m-tolyl ether,*

$$C_6H_4Me \cdot O \cdot C_6H_3Me \cdot NO_2,$$
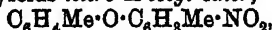
b. p. 245—250°/50 mm., m. p. 48°, which on reduction with iron and acetic acid gives the corresponding *amine,* giving a violet coloration with calcium chloride. If during the nitration the temperature rises to 80—90°, *dinitro-m-tolyl ether,* $O(C_6H_3Me \cdot NO_2)_2$, prisms, m. p. 112°, is obtained, in which the nitro-groups are probably para to the oxygen.

By gradually adding tolyl ether to fuming nitric acid, kept cold, and then adding water, a paste is obtained, which, after extraction of the above dinitro-compound, is added to a mixture of sulphuric and nitric acids and yields 2 : 4 : 2′ : 4′-*tetranitro-m-tolyl ether,*
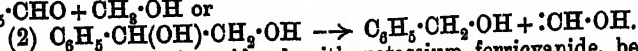
$$O[C_6H_2Me(NO_2)_2]_2,$$
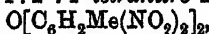
a white, amorphous powder, m. p. 203°, which on boiling with concentrated aqueous potassium hydroxide yields *dinitrodihydroxy-m-tolyl ether,* a black, crystalline powder, m. p. 300° (decomp.).

If the original tolyl ether is nitrated in sulphuric acid solution by the gradual addition of fuming nitric acid, the temperature being gradually raised to 90° towards the end of the reaction, 2 : 6 : 2′ : 6′-*tetranitro-m-tolyl ether,* hexagonal plates, m. p. 147°, is obtained together with a large proportion of its isomeride. Attempts to carry the nitration further have, as yet, not been successful.   W. G.

Preparation and Oxidation of Styrolene Alcohol [Phenylethylene Glycol]. WM. LLOYD EVANS and LOU HELEN MORGAN (*J. Amer. Chem. Soc.*, 1913, 35, 54—68).—This investigation was undertaken with the object of determining the mechanism of the oxidation of phenylethylene glycol (styrolene alcohol) with different reagents, and of establishing the conditions under which mandelaldehyde might be isolated as an intermediate product. Zincke (*Annalen*, 1883, 216, 303) has shown that on oxidising the glycol with chromic acid, benzaldehyde, formaldehyde, and formic acid are produced, that with potassium permanganate a quantitative yield of benzaldehyde may be obtained, and that with nitric acid, benzoylcarbinol and benzoylformic acid are formed.
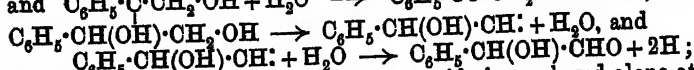
Phenylethylene glycol is best prepared by the hydrolysis of the corresponding diacetate (Zincke, *loc. cit.*). On oxidation with potassium permanganate, either alone or in presence of alkali hydroxide, it yields benzoic acid, but not phenylglyoxylic acid, the reaction taking place

in accordance with the equation: (1) $C_6H_5\cdot CH(OH)\cdot CH_2\cdot OH \longrightarrow$
$C_6H_5\cdot CHO + CH_3\cdot OH$ or
(2) $C_6H_5\cdot CH(OH)\cdot CH_2\cdot OH \longrightarrow C_6H_5\cdot CH_2\cdot OH + :CH\cdot OH.$
When the glycol is oxidised with potassium ferricyanide, benzoic
acid is the chief product, but mandelic acid is not formed, and the
reaction proceeds according to equation (1) or (2)   With silver oxide,
in presence of alkali hydroxide, the oxidation takes place, with formation
of benzoylcarbinol as the first product of the reaction, in one of the follow-

ing ways: (3) $C_6H_5\cdot CH(OH)\cdot CH_2\cdot OH \longrightarrow C_6H_5\cdot \overset{|}{C}\cdot CH_2\cdot OH + H_2O$;

and $C_6H_5\cdot \overset{|}{C}\cdot CH_2\cdot OH + H_2O \longrightarrow C_6H_5\cdot CO\cdot CH_2\cdot OH + 2H$;   or   (4)
$C_6H_5\cdot CH(OH)\cdot CH_2\cdot OH \longrightarrow C_6H_5\cdot CH(OH)\cdot CH: + H_2O$, and
$C_6H_5\cdot CH(OH)\cdot CH: + H_2O \longrightarrow C_6H_5\cdot CH(OH)\cdot CHO + 2H$;
at 60°, both reactions occur.   If silver oxide is employed alone at 20°,
the reaction seems to proceed entirely in accordance with equation (3).
The oxidation of phenylethylene glycol by bromine in presence of
potassium carbonate yields benzoylcarbinol.   Aqueous solutions of
copper salts do not exert any marked action on the glycol even
at 100°.   E. G.

Preparation of Benzyl Mercaptan.   JOHN A. SMYTHE (*Proc.
Univ. Durham, Phil. Soc.*, 1912, 4, !220—222).—Benzyl mercaptan
may be prepared from benzyl sulphide by reduction with iron filings in
acetic acid solution.   When dissolved in glacial acetic acid, and the
solution saturated simultaneously with hydrogen chloride and sulphur
dioxide, it yields benzyl disulphide and trisulphide in equal amounts.
   F. B.

Derivatives of Ethylene Dimercaptan, $SH\cdot CH_2\cdot CH_2\cdot SH$,
s-Dithiolethylene, $SH\cdot CH:CH\cdot SH$, and of Dithiolacetylene,
$SH\cdot C:C\cdot SH$.   EMIL FROMM, HANS BENZINGER, and FRITZ SCHAFER
(*Annalen*, 1912, **394**, 325—337).—s-*Diethylthiolethylene*,
                                        $SEt\cdot CH:CH\cdot SEt$,
b. p. 170°/13 mm., is obtained by the slow addition of dichloroethylene
to ethyl mercaptan and potassium hydroxide in alcohol, the mixture
being finally heated on the water-bath.   The addition of dichloro-
ethylene to benzyl mercaptan in boiling 7·5% alcoholic potassium
hydroxide yields s-*dibenzylthiolethylene*, $C_{16}H_{16}S_2$, m. p. 61°, colourless
needles, which decomposes by heating into hydrogen sulphide, toluene,
benzyl mercaptan, and stilbene, and forms a *dibromide*, $C_{16}H_{16}Br_2S_2$,
m. p. 73—74°, with bromine in carbon disulphide.   By heating with
alcoholic potassium hydroxide, this dibromide yields *dibenzylthiol-
acetylene*, $CH_2Ph\cdot S\cdot C:C\cdot S\cdot CH_2Ph$, m. p. 53°, straw-yellow needles or
flesh-coloured leaflets.
    s-*Dibenzylthiolethane*, $CH_2Ph\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot CH_2Ph$, m. p. 38°, pre-
pared from ethylene dibromide and sodium benzyl mercaptide, is
oxidised by cold nitric acid (D 1·34) to the *disulphoxide*, $C_{16}H_{18}O_2S_2$,
m. p. 198°, white leaflets; the *disulphone*, $C_{16}H_{18}O_4S_2$, pearly leaflets
subliming at 304°, is obtained by oxidising the disulphoxide by
5% potassium permanganate, or the sulphide by chromic and acetic
acids.

s-*Di*-o-*nitrophenylthiolethylene*, $C_{14}H_{10}O_4N_2S_3$, m. p. 215°, golden-yellow leaflets, prepared from dichloroethylene, o-nitrophenyl mercaptan, and alcoholic potassium hydroxide, forms a *dibromide*,

$$C_{14}H_{10}O_4N_2Br_2S_2,$$
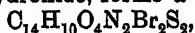
m. p. 132°, citron-yellow prisms, which is converted into *di*-o-*nitrophenylthiolacetylene*, m. p. 225°, yellow needles, by hot alcoholic potassium hydroxide. This acetylene derivative absorbs only one mol. of bromine in chloroform, forming *dibromodi*-o-*nitrophenylthiolethylene*, $C_2Br_2(S\cdot C_6H_4\cdot NO_2)_2$, m. p. 209°, yellow leaflets. Sodium o-nitrophenyl mercaptide and di-o-nitrophenylthiolethylene dibromide react in alcohol to form *glyoxaltetra*-o-*nitrophenylmercaptal*,

$$CH(S\cdot C_6H_4\cdot NO_2)_2\cdot CH(S\cdot C_6H_4\cdot NO_2)_2,$$
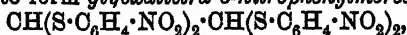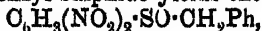
yellow needles, m. p. 178°.

s - *Di* - o - *aminophenylthiolethylene*, $C_2H_2(S\cdot C_6H_4\cdot NH_2)_2$, m. p. 67°, colourless leaflets, obtained by the reduction of the nitro compound by alkaline sodium hyposulphite, forms a *dibenzoyl* derivative, m. p. 132°, *diacetyl* derivative, m. p. 159°, and a sparingly soluble *dihydrochloride*, m. p. 201°; the last reacts with only one mol. of sodium nitrite during its diazotisation.

s-*Di*-o-*nitrophenylthiolethane*, $C_2H_4(S\cdot C_6H_4\cdot NO_2)_2$, m. p. 207°, yellow prisms, prepared by treating moist o-nitrophenyl mercaptan and ethylene dibromide with hot alcoholic potassium hydroxide, is oxidised to the *disulphoxide*, $C_{14}H_{12}O_6N_2S_2$, m. p. 145°, pale yellow needles, by chromic and warm glacial acetic acids, and to the *disulphone*, m. p. 164°, almost colourless prisms, by chromic and boiling glacial acetic acids, and yields s-*di*-o-*aminophenylthiolethane*, m. p. 74° (*dibenzoyl* derivative, m. p. 153°; *diacetyl* derivative, m. p. 194—195°), by reduction with tin and hydrochloric acid.

s-*Di*-p-*nitrophenylthiolethylene*, m. p. 126°, prepared like the ortho-isomeride, forms a *dibromide*, $C_{14}H_{10}O_4N_2Br_2S_2$, m. p. 137°, yellow needles, and yields by reduction the *diamino*-compound (*diacetyl* derivative, m. p. 194°), which can be readily tetrazotised. s-*Di*-p-*nitrophenylthiolethane*, m. p. 134°, crystallises in yellow prisms.

Di-2 : 4-*dinitrophenyl disulphide*, $S_2[C_6H_3(NO_2)_2]_2$, yellow needles, exploding at 280°, is obtained by heating alcoholic 2 : 4-dinitrochloro-benzene with aqueous sodium sulphide and sulphur.

2 : 4-Dinitrophenyl benzyl sulphide yields the *sulphoxide*,

$$C_6H_3(NO_2)_2\cdot SO\cdot CH_2Ph,$$

m. p. 144° (decomp.), straw-yellow needles, by oxidation with 30% hydrogen peroxide in glacial acetic acid, and the *sulphone*, m. p. 177°, by oxidation with chromic and warm glacial acetic acids.

2 : 4-*Dinitrophenyl methyl sulphide*, m. p. 126°, prepared from 2 : 4-dinitrophenyl mercaptan, methyl iodide, and methyl alcoholic sodium methoxide, yields the *sulphoxide*, m. p. 159°, yellow leaflets, and the *sulphone*, m. p. 184° (decomp.), colourless needles, by oxidation with hydrogen peroxide and chromic acid respectively.   C. S.

Decomposition of Benzyl Disulphide by Alkalis. EMIL FROMM and AQUILA FORSTER (*Annalen*, 1912, 394, 338—343).—In addition to the substances identified by Price and Twiss among the products of decomposition of benzyl disulphide by alkalis (T., 1910, 97,

1175), the authors have detected thiobenzoic acid and dithiobenzoic acid. *Benzyl dithiobenzoate*, $Ph \cdot CS_2 \cdot CH_2Ph$, m. p. 55°, is prepared by heating the acid and benzyl chloride with alcohol and 10% sodium hydroxide.

When the preceding decomposition is effected in the presence of benzyl chloride, the authors could obtain only about 5% of the benzyl-mercaptal of benzaldehyde instead of 50%, as stated by Price and Twiss (*loc. cit.*), and they suggest that the latters' benzyl chloride was highly contaminated with benzylidene chloride, which reacts with the sodium benzyl mercaptide to form the benzylmercaptal.

[With MAX KLINGER.]—The substance, m. p. 164°, obtained by Fromm and Schmoldt by the dry distillation of benzoyl sulphide, benzoyl disulphide, or thiobenzoic acid, and stated to be tolane tetra-sulphide (A., 1907, i, 702), is now shown to be a mixture. By treatment with ammonium sulphide or with ether and petroleum, it is separated into sulphur and tetraphenylthiophen, m. p. 184°. The substance described as tolane disulphide (*loc. cit.*) is probably also a mixture of sulphur and tetraphenylthiophen.   C. S.

Some Mercaptals and Mercaptols and their Derivatives. EMIL FROMM, AQUILA FORSTER, and BORIS VON SCHERSCHEWITZKI (*Annalen*, 1912, 394, 343—349).—The *benzylmercaptal* of formaldehyde, $CH_2(S \cdot CH_2Ph)_2$, m. p. 55°, obtained by saturating with hydrogen chloride a solution of benzyl mercaptan and excess of 40% formaldehyde in glacial acetic acid, is oxidised to the *sulphoxide*, $CH_2(SO \cdot CH_2Ph)$, m. p. 189°, by hydrogen peroxide and to the *sulphone*, $CH_2(SO_2 \cdot CH_2Ph)_2$, m. p. 216°, by acidified 5% potassium permanganate. The *benzylmercaptal* of acetaldehyde,

$$CHMe(S \cdot CH_2Ph)_2,$$

b. p. 200—205°/5 mm., is oxidised to the *sulphone*, $CHMe(SO_2 \cdot CH_2Ph)_2$, m. p. 176°, by 5% potassium permanganate.

The *benzylmercaptole* of acetone, $CMe_2(S \cdot CH_2Ph)_2$, b. p. 195°/5 mm., yields the *sulphoxide*, m. p. 105°, and *sulphone*, m. p. 125°, by oxidation as above. This sulphone and also αα-dibenzylsulphone-ethane are produced when dibenzylsulphonemethane is heated with alcoholic methyl iodide and aqueous sodium hydroxide. When αα-dibenzylsulphonepropane is similarly treated, benzylmethylsulphone is obtained, owing to the intermediate formation of benzylsulphinic acid. The following substances are also described : the p-*tolylmercaptal* of formaldehyde and its *sulphoxide*, m. p. 45°, and *sulphone*, m. p. 135°; the p-*tolylmercaptole* of acetone, m. p. 64—65°, and its *sulphoxide*, m. p 75—76°, and *sulphone*, m. p. 147—148°; αα-*di* p-*tolylsulphone-ethane*, m. p. 156°, and αα-*di-p-tolyl-sulphonepropane*, m. p. 189°.   C. S.

Catalysis of Dehydrogenation of Hexahydrobenzoic [*cyclo*-Hexanecarboxylic] Acid. NICOLAI D. ZELINSKI and N. UKLONSKAJA (*Ber.*, 1912, 45, 3677—3678).—An extension of the process which proved successful with *cyclo*hexane and its methyl derivative to simple derivatives which are not hydrocarbons (Zelinski, A., 1911, i, 958).

When *cyclo*hexanecarboxylic acid is added gradually to palladium

black at 300° in an atmosphere of hydrogen at 20—25 mm. pressure, the vapours which pass away on condensation give crystals of benzoic acid in a smaller quantity of unchanged liquid *cyclo*hexanecarboxylic acid.

If ethyl *cyclo*hexanecarboxylate (b. p. 195—197°, n^{17} 1·4424) is submitted twice to the above treatment, the liquid product can be separated by distillation into two fractions, the smaller one consisting of a mixture of ethyl benzoate and ethyl benzoate (n^{18} 1·5071), whilst the main fraction is of pure ethyl *cyclo*hexanecarboxylate. The progress of the dehydrogenation can be conveniently followed by the change in the refractive index.

As with *cyclo*pentane and its methyl derivative, no dehydrogenation was observed when methyl*cyclo*pentanecarboxylic acid was treated in a similar manner. D. F. T.

Study of Double Linkings. ANTONIO MADINAVEITIA and JOSÉ SUREDA BLANES (*Anal. Fis. Quim.*, 1912, 10, 381—389).—Under the influence of platinum black, cinnamic acid in glacial acetic acid solution is fully hydrogenised to Zelinski's *cyclo*hexylpropionic acid, whilst palladium black and colloidal palladium determine reduction to phenyl-propionic acid. *Octahydroeugenole*, prepared by the hydrogenation of eugenole with platinum black as catalyst, has b. p. 125° at 12 mm., and forms an oil soluble in acetic acid, alcohol and ether, and insoluble in water and light petroleum. In the presence of palladium black, eugenole is reduced to hydroeugenole. G. D. L.

Some Para-derivatives of Phenylacetic Acid. S. ROBSON (*Proc. Univ. Durham Phil. Soc.*, 1912, 4, 225—227).—*p*-Bromophenyl-acetic acid, m. p. 114—115°, has been prepared from *p*-nitrophenyl-acetonitrile by reduction with stannous chloride, followed by replace-ment of the amino-group by bromine by means of the diazo-reaction, and finally hydrolysing the resulting *p*-bromophenylacetonitrile, m. p. 112°, with sulphuric acid; on nitration it yields 4-bromo-3-nitro-phenylacetic acid (Bedson, T., 1880, 37, 100).

p-Chloro- and *p*-iodo-phenylacetic acids have been prepared in a similar manner. F. B.

Walden's Inversion and Substitution Processes. II. EMIL FISCHER (*Annalen*, 1912, 394, 350—362. Compare A., 1911, i, 418). —Mainly a reply to Biilmann (A., 1912, i, 420) and to Noyes and Potter (*ibid.*, 786).

Phenylpropiolic acid is reduced to cinnamic acid by zinc dust in alkaline as well as in acid solution (compare A., 1912, i, 187); conse-quently, the presence of the acid is not the cause of the presumably abnormal course of the reduction. C. S.

Behaviour Towards Light of Cinnamylideneacetonitrile of α-Phenylcinnamylideneacetic Acid, and of the Two Cinn-amylideneacetic Acids. HANS STOBBE [and NICOLAUS BARBA-SCHINOV] (*Ber.*, 1912, 45, 3396—3408).—When the dark yellow

α-phenylcinnamylideneacetonitrile, $CHPh\!:\!CH\cdot CH\!:\!CPh\cdot CN$, is exposed to light in benzene or chloroform solution, a resin is formed, together with benzoic acid and a colourless dimeride, $C_{34}H_{26}N_2$, m. p. 197°. It thus behaves very similarly to cinnamylidenemalonic acid (Rüber, A., 1902, i, 617), which is polymerised by light to diphenyltetramethyl-enediethenyldicarboxylic [diphenyl*cyclo*butyldiacrylic] acid. The dimeride, when cautiously oxidised by potassium permanganate in aqueous alkaline methylacetate solution, is converted into benzoyl cyanide and α-truxillic acid, $CO_2H\cdot CH{<}^{CHPh}_{CHPh}{>}CH\cdot CO_2H$. This establishes the dimeride as 1 : 3-*diphenyltetramethylene*-2 : 4-*diethenyl-β-phenyl-β-cyanide* [1 : 3-*diphenylcyclobutane*-2 : 4-*diatroponitrile*],

$$CN\cdot CPh\!:\!CH\cdot CH{<}^{CHPh}_{CHPh}{>}CH\cdot CH\!:\!CPh\cdot CN.$$

It combines with bromine to a colourless tetrabromide, indicating the absence of a conjugated double bond system, whereas phenylcinnamyl-idene acetic acid forms only a colourless dibromide. The polymerisation of the cyanide is accompanied by bleaching, the absorption field of the dimeride being displaced some 800 wave-lengths towards the ultra-violet.

On heating at 200°, the dimeride is depolymerised, yielding simply unimolecular cyanide. This behaviour, which is shared by α-truxillic acid, is not in accordance with that of other *cyclo*butane derivatives, and throws some uncertainty on the four-ring formulæ adopted.

A second colourless dimeride, m. p. 215°, is formed during exposure to light. This is also produced as a by-product of the action of bromine on the first dimeride. It does not unite with bromine, and it is not so easily depolymerised ; the constitution has not been determined.

α-Phenylcinnamylideneacetic acid, whether used in the form of the acid, its sodium salt or methyl ester, is stable towards light in the absence of oxygen, but in presence of air it is oxidised to benzalde-hyde and benzoic acid. No polymerisation product is formed. The methyl ester is more readily oxidised than the acid, whilst the sodium salt is still more resistant.

Similarly under no conditions could a polymeride be obtained from the isomeric cinnamylideneacetic acids. Some oxidation takes place, also the *allo*-acid is converted into its isomeride.

The dimeric acid, $C_{22}H_{20}O_4$, obtained by Rüber (*loc. cit.*) on heating the dimeride of cinnamylidenemalonic acid could not be depolymerised to cinnamylideneacetic acid. The sodium salt and methyl ester behave similarly to the acid ; the ester is more easily oxidised under the influence of light ; the salt is more stable than the acid. The different behaviour of the compounds studied is not due to any differences in the selective absorption of light by them.

The *dibromide*, $C_{17}H_{13}NBr_2$, from phenylcinnamylideneacetonitrile, crystallises in colourless needles, m. p. 118°. The *tetrabromide* $C_{34}H_{26}N_2Br_4$, of the dimeride has m. p. 276°.

Cinnamylidenemalonic acid forms a *dibromide*, $C_{12}H_{10}O_4Br_2$, m. p. 180°. The *tetrabromide* of the dimeride has decomp. above 100°.

Methyl allo*cinnamylideneacetate* is an oil, solidifying below $-80°$.

E. F. A.

Some Pharmaceutical Incompatibilities of Salol [Phenyl Salicylate]. ITALO BELLUCCI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 610—616. Compare Caille, A., 1909, i, 594).—In pharmaceutical practice it is not infrequently observed that two dry, solid drugs yield a pasty or liquid mixture. This phenomenon is not due in all cases to the occurrence of a chemical reaction, but results in some cases from the formation of an eutectic mixture of low m. p. In the present paper the author gives tables and curves which exhibit the results of the thermal analysis of the binary mixtures of salol with the substances mentioned in the following list:
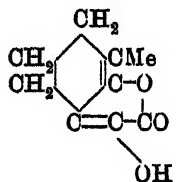
	Eutectic.			Eutectic.	
	Temp.	% Salol.		Temp.	% Salol.
β-Naphthol	34°	90	Chloral hydrate .	17°	61
Antipyrine	30	83	Thymol	13	66
Urethane	29	86	Camphor	6	56
Menthol	28	45	Guaiacol	3	53
β-Bromocamphor.,	21	64			

In the system salol-menthol there is complete miscibility in the solid state, the curve being Roozeboom's type III. with a minimum at about 28° and 45% of salol. From the temperature given it follows that some of the above binary mixtures are pasty at ordinary temperatures, others liquid. R. V. S.
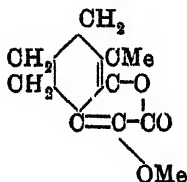
Condensation of Cyclic Ketones with Ethyl Oxalate. ARTHUR KOTZ, K. BLENDERMANN, and J. MEYER (*Ber.*, 1912, 45, 3702—3705. Compare A., 1906, 88, 668).—Active 1-methyl*cyclo*hexan-3-one condenses in the cold with ethyl oxalate and sodium ethoxide, and when the dry product is treated with methyl iodide and subsequently hydrolysed, 1 : 4-dimethyl*cyclo*hexan-2-one is obtained, b. p. 51°/ 10 mm. Its *oxime*, $C_8H_{15}ON$, has m. p. 97—98°.

Inactive 1-methyl*cyclo*hexan-2-one condenses to form a *methylcyclohexenolpyruvolactone*, $C_9H_{10}O_3$, m. p. 141°, alcohol being eliminated. When this is treated with methyl iodide, a *dimethyl* compound, $C_{10}H_{12}O_3$, m. p. 87°, is formed, which absorbs 4 atoms of hydrogen and yields 1-methyl*cyclo*hexan-2-one on hydrolysis. Since these compounds give no reactions for ketones, and since Claisen has shown that the formation of lactones is possible in such circumstances (A., 1895, i, 373), they may be represented by the annexed formulæ. J. C. W.

Melting Point of Ethyl Gallate. HENRY C. BIDDLE (*J. Amer. Chem. Soc.*, 1913, 35, 96).—Biddle and Kelley (A., 1912, i, 714) suggested that the peculiar behaviour of ethyl gallate on melting might be due to the existence of two crystalline forms. It has now been found, however, that by continued purification the ester can

be obtained in long, colourless needles, melting fairly sharply at 160°.

<div align="right">E. G.</div>

Kojic Acid, a New Organic Acid Formed by Aspergillus oryzæ. T. YABUTA (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, **5**, 51—58).—*Kojic acid*, $C_{10}H_6(OH)_4(CO_2H)_2$, obtained from finely powdered *Aspergillus oryzae*, forms colourless needles or prisms, m. p. 152°. The acid gives a strong red colour with ferric chloride; it has no action on alkaline diazobenzenesulphonic acid, on Millon's reagent, or on Fehling's solution. The aqueous solution absorbs much bromine. Methoxyl and ethoxyl groups are not present. The *copper* salt, $C_{12}H_{12}O_8Cu$, forms light green, rhombic crystals. The *acetyl* derivative, $C_{12}H_{10}O_4(OAc)_4$, crystallises from alcohol in colourless needles, m. p 102°. The *dibenzoyl* derivative, $C_{12}H_{10}O_4(OH)_2(OBz)_2$, m. p. 137°, and the *tetrabenzoyl* derivative, $C_{12}H_{10}O_4(OBz)_4$, m. p. 135°, were prepared.

The acid also occurs in *Aspergillus albus, A. candidus*, and *A. nidulans*, but was not found in thirteen other varieties or in *Penicillium* or *Mucor*.

The production of the acid seems to depend on the food supplied to the *Aspergillus*. It was found in *Aspergillus* grown on certain cereals and potatoes, but not with leguminous seeds.

<div align="right">N. H. J. M.</div>

Synthesis of β-Glucosidogallic Acid. EMIL FISCHER and HERMANN STRAUSS (*Ber.*, 1912, **45**, 3773—3779).—Ethyl gallate combines with acetobromoglucose, forming *ethyl tetra-acetylglucosidogallate*, which is completely hydrolysed by cold barium hydroxide solution to *glucosidogallic acid*, $C_6H_{11}O_5 \cdot C_6H_2(OH)_2 \cdot CO_2H$. This crystallises in colourless, interlaced needles, m. p. 193° (decomp.), after sintering from 155°, $[\alpha]_D^{20} - 22°$. It is monobasic and is hydrolysed by emulsin into dextrose and gallic acid. With ferric chloride a brownish-red coloration is produced, indicating that the *p*-hydroxyl group of the gallic acid is attached to the sugar residue. It differs from the supposed glucosides of gallic acid described by Gibson (A., 1903, i, 355) and by Feist (A., 1912, i, 566, 888).

Ethyl tetra-acetylglucosidogallate crystallises in colourless needles, m. p. 180—181° (corr.), $[\alpha]_D^{20} - 10 \cdot 6°$.

<div align="right">E. F. A.</div>

Some Reduction Products of Ellagic Acid. MAXIMILIAN NIERENSTEIN and FREDERIC W. RIXON (*Annalen*, 1912, **394**, 249—258). —The electrolytic reduction of ellagic acid in a divided cell with mercury cathode and nickel anode yields different products at different temperatures. By reduction in $4N$-sodium hydroxide at the ordinary temperature, ellagic acid yields chiefly *leucoellagic acid*,

$$C_6H(OH)_2 \underset{O \cdot CH(OH)}{\overset{CH(OH) \cdot O}{<}} \rangle C_6H(OH)_2,$$
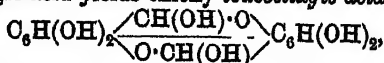
m. p. 294—296° (decomp.), small needles. This substance is colourless, does not possess any tinctorial properties, forms a *hexa-acetyl* derivative, m. p. 272—275° (decomp.), and a *hexabenzoyl* derivative, m. p. 300—305° (decomp.), and is reconverted into ellagic acid by oxidation with hydrogen peroxide. By boiling with aqueous potassium hydroxide and carbon tetrachloride, leucoellagic acid is converted into the

potassium salt, long rhombohedra, of the *dicarboxylic acid*,

$$CO_2H \cdot C_6(OH)_2 \overset{CH(OH) \cdot O}{\underset{O \cdot CH(OH)}{<}{>}} C_6(OH)_2 \cdot CO_2H,$$
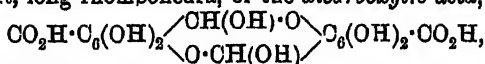
m. p. 123—124° (decomp.), small needles. A solution of the dicarboxylic acid in ethyl acetate has been separated by strychnine into the two (impure) active acids and the meso-modification. The impure d-*acid* has m. p. 122—124° and $[\alpha]_D^{17} +19 \cdot 9°$; the impure l-*acid* has m. p 127—131° and $[\alpha]_D^{17} - 2 \cdot 3°$, and the meso-*acid* has m. p. 143—146° (decomp.).

The electrolytic reduction of ellagic acid in alkaline solution at 70° yields pentahydroxydiphenylmethylolide (A., 1908, i, 548), whilst its reduction in concentrated sodium hydroxide at 110° yields 2 : 3 : 4 : 2' : 3' : 4'-hexahydroxydiphenyl. C. S.

New Basic Component of the Muscle of the Dog and Its Relation to Hexamethylornithine. DANKWART ACKERMANN (*Zeitsch. Biol.*, 1912, 59, 433—440).—*Myokynine*, a basic substance obtained from dog's muscle, is probably *l*-hexamethylornithine. Both substances give precipitates with phosphotungstic acid and with alcoholic mercuric chloride solution.

The *aurichloride* from myokynine contains $2H_2O$ and is lævorotatory, that from *hexamethylornithine*, m. p. 201—205°, is anhydrous. Myokynine *platinichloride* $(2H_2O)$ has m. p. 232—234°; the isomeride (H_2O) has m. p. 232—233°.

Hexamethylornithine is obtained from ornithine by means of methyl sulphate ; it is dextrorotatory. E F. A.

The Bromination of cycloPentanone. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1912, 155, 1522—1524).—When bromine (4 mols.) dissolved in carbon tetrachloride is added to a solution of cyclopentanone (1 mol.) in the same solvent, either with or without the presence of aluminium bromide, the mixture being kept cold, there is obtained, on evaporating off the solvent, an abundant crop of crystals with more or less oil. The crystals are separated, and on purification yield *tetrabromocyclopentanone*, $C_5H_4OBr_4$, large plates, m. p. 99°. It is very soluble in ether, ethyl acetate, etc., and when left to itself slowly loses hydrogen bromide and is converted into a yellow oil. This change takes place rapidly in solution in ethyl acetate, and the product when purified is *tribromocyclopentanone*, $C_5H_3OBr_3$, colourless prisms, m. p. 57—58°. This substance on bromination in carbon tetrachloride solution adds on two atoms of bromine, giving *pentabromocyclopentanone*, $C_5H_3OBr_5$. m. p. 93°.

The oil obtained in the original bromination slowly loses hydrogen bromide, and on boiling the product with water and extracting with ether, a *compound* is obtained, m. p. 147°, which analysis shows to be either $C_5H_3O_2Br$ or $C_5H_5O_2Br$, the amount of material to hand not allowing of definite distinction between the two formulæ. The substance functions both as an alcohol and a ketone. W. G.

2 : 2-Dimethylcycloheptanone. P. JOSEPH TARBOURIECH (*Compt. rend.*, 1913, 156, 75—77).—The dehydration of cyclohexanoldimethylcarbinol gives rise to a hydrocarbon, C_9H_{14}, and two isomeric ketones,

$C_9H_{16}O$, one of which has been shown to be 1-acetyl-1-methyl*cyclo*hexane (compare A., 1910, i, 557), and the other is now proved to be 2 : 2-*dimethyl*cyclo*heptanone*, $Me_2C{<}^{CH_2 \cdot CH_2 \cdot CH_2}_{CO-CH_2-CH_2}$, the :CO group having been introduced into the hexatomic ring. By purification through its oxime, it is obtained as a colourless liquid, b. p. 82°/ 18 mm., giving a *carbanilino-oxime*, m. p. 94°, and a *semicarbazone*, m. p. 176°. On oxidation with weak alkaline permanganate, it yields *α-keto-ββ-dimethylpimelic acid*, $CO_2H \cdot CO \cdot CMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, m. p. 67°, giving a *semicarbazone*, m. p. 185°, and an *oxime*, m. p. 140—141°, which on heating further decomposes, losing carbon dioxide and water, giving *δ-cyano-δδ-dimethylpentoic acid*,
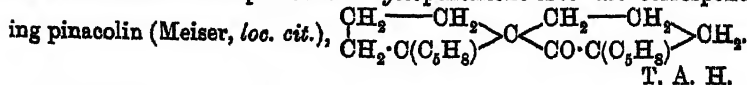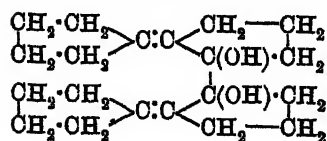$$CN \cdot CMe_2 \cdot [CH_2]_3 \cdot CO_2H,$$
m. p. 34—35°, which on hydrolysis with alcoholic potassium hydroxide is converted into *αα*-dimethyladipic acid.   W. G.

Electrolysis of *cyclo*Pentanone. MARCEL GODCHOT and FÉLIX TABOURY (*Bull. Soc. chim.*, 1913, [iv], 13, 12—17. Compare A., 1912, i, 34, 552).—On electrolysis in alkaline solution, *cyclo*pentanone yields *cyclo*pentylidene*cyclo*pentanone (Wallach, A., 1897, i, 160) and two other products, which appear to be tetra*cyclo*pentane derivatives. It is probable that the *cyclo*pentylidene*cyclo*pentanone is formed by the condensation of two mols. of *cyclo*pentanone in presence of alkali, and that the other two products are formed from the condensation product by electrolytic action, the first being the corresponding pinacone and the second the corresponding pinacolin. These supposed tetra*cyclo*pentane derivatives have the following characters. The first, m. p. 160—162°, has the formula $C_{20}H_{30}O_2$, and is probably identical with the substance obtained by Meiser (A., 1899, i, 741).

$CH_2 \cdot CH_2{>}C{:}C{<}^{CH_2—CH_2}_{C(OH) \cdot CH_2}$
$CH_2 \cdot CH_2$

$CH_2 \cdot CH_2{>}C{:}C{<}^{C(OH) \cdot CH_2}_{CH_2—CH_2}$
$CH_2 \cdot CH_2$

It probably has the annexed constitution, which makes it the pinacone corresponding with *cyclo*pentylidene*cyclo*pentanone. This substance probably loses 1 mol. of water, giving rise to the second *product*, $C_{20}H_{28}O$, b. p. 320°/25 mm., a yellow liquid which gives no typical carbonyl derivatives, although it probably has the following constitution, being formed in a manner analogous to the transformation of the pinacone of *cyclo*pentanone into the corresponding pinacolin (Meiser, *loc. cit.*), $^{CH_2—CH_2}_{CH_2 \cdot C(C_5H_8)}{>}C{<}^{CH_2—CH_2}_{CO \cdot C(C_5H_8)}{>}CH_2$.
                                                                T. A. H.

Terpenes and Ethereal Oils. CXII. Condensation Products of Cyclic Ketones and Acetone. OTTO WALLACH and WOLFGANG VON RECHENBERG (*Annalen*, 1912, 394, 362—384).— Many years ago a substance, $C_{10}H_{16}O$, isomeric with pulegone, was obtained by the condensation of acetone and methyl*cyclo*hexan-3-one, but its constitution could not be definitely settled (A., 1896, i, 310 ; 1898, i, 484). An extensive examination of similar condensations now leads to the generalisation that the acetone attacks the carbonyl group of *cyclo*hexanones, but a nuclear methylene group of *cyclo*-

pentanones; thus equal molecular quantities of *cyclo*pentanone and acetone are kept in alcoholic sodium ethoxide for some hours at 0°, and then for two to three days at the ordinary temperature, whereby, in addition to a little mesityl oxide, *propylidenecyclopentan 2-one*,

$$CMe_2{:}C\overset{CO-CH_2}{\underset{CH_2\cdot CH_2}{<}},$$
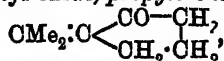
b. p. 195—199°, D^{20} 0·9565, n_D^{20} 1·4932, is obtained (*semicarbazone*, m. p. 215—218°; *oxime*, m. p. 77°), by the reduction of which by hydrogen and colloidal palladium, iso*propyl*cyclo*pentan-2-one*, b. p. 176·5—177·5°, D^{21} 0·9000, n_D^{21} 1·4419 (*semicarbazone*, m. p. 197°; *benzylidene* derivative, m. p. 79—80°), is formed. In a similar manner, i-*methyl*cyclo*pentan-3-one*, b. p. 144—144·5°, D^{22} 0·913, n_D 1·4329 (*semicarbazone*, m. p. 185°, *benzylidene* derivative, m. p. 157°; m-*nitrobenzylidene* derivative, m. p. 174°; *anisylidene* derivative, m. p. 197—198°; *piperonylidene* derivative, m. p. 166—167°; *cinnamylidene* derivative, m. p. 148° [compare A., 1904, i, 752; 1908, i, 424]), prepared from i-β-methyladipic acid, condenses with acetone to form 1-*methyl-4-propylidene*cyclo*pentan-3-one*,　$CMe_2{:}C\overset{CH_2\cdot CHMe}{\underset{CO-CH_2}{<}}$, b. p.

203—205°, D^{21} 0·9315, n_D^{21} 1·4846 (*semicarbazone*, m. p. 210°; *oxime*, m. p. 89°). The constitution of this compound is determined by its exalted molecular refraction, and by the fact that 1-*methyl*-4-iso*propyl*-cyclo*pentan-3-one*, b. p. 186—187°, D^{20} 0·8850, n_D^{20} 1·4392 (*semicarbazone*, m. p. 179°; *oxime*, m. p. 66°), obtained from it by Paal's method, yields by oxidation with chromic and dilute sulphuric acids a *keto-acid*, $CHMe_2\cdot CO\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2H$ (*semicarbazone*, m. p. 164°; *oxime*, m. p. 76—77°), by the further oxidation of which i-β-methylglutaric acid is produced.

*cyclo*Hexanone and acetone condense to form Δ¹-cyclo*hexenylacetone*, $C_6H_9\cdot CH_2\cdot COMe$, b. p. 203—204°, D^{19} 0·9375, n_D 1·4736 (*semicarbazone*, m. p. 144—145°; *oxime*, b. p. 135°/20 mm.), the constitution of which follows from its molecular refraction and from its reduction by Paal's method to *cyclo*hexylacetone, m. p. 171—172° (not 165—166°, A., 1907, i, 616). *cyclo*Hexyl*trimethylcarbinol*, $C_6H_{11}\cdot CH_2\cdot CMe_2\cdot OH$, b. p. 208°, D^{20} 0·902, n_D^{20} 1·4627, is prepared from *cyclo*hexylacetone and magnesium methyl iodide in the usual manner.

Methyl*cyclo*hexan-4-one and acetone yield 1-*methyl*-Δ³-cyclo*hexenyl*-4-*acetone*, $C_6H_8Me\cdot CH_2\cdot COMe$, b. p. 216—217°, D^{21} 0·916, n_D^{21} 1·4672 (*semicarbazone*, m. p. 122—123°), by the reduction of which 1-*methyl*-cyclo*hexyl*-4-*acetone*, b. p. 214—215°, D^{21} 0·8930, n_D^{21} 1·4499 (*semicarbazone*, m. p. 166°), is formed.

The compound $C_{10}H_{16}O$, obtained from active methyl*cyclo*hexan-3-one and acetone (*loc. cit.*), is now proved to be 1-*methyl*-Δ²⁽ᵒʳ ³⁾-cyclo*hexenyl-3-acetone*, $C_6H_8Me\cdot CH_2\cdot COMe$, or a mixture of both. By reduction by Paal's method, it yields 1-*methyl*cyclo*hexyl-3-acetone*, $C_6H_{10}Me\cdot CH_2\cdot COMe$, b. p. 212—214°, $D^{21·5}$ 0·8915, $n_D^{21·5}$ 1·4496 (*semicarbazone*, m. p. 154°), which is converted by alkaline hypobromite into 1-methyl*cyclo*hexyl-3-acetic acid, and by magnesium methyl iodide ultimately into 1-*methyl*cyclo*hexyltrimethylcarbinol*,

$$C_6H_{10}Me\cdot CH_2\cdot CMe_2\cdot OH,$$
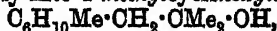
b. p. 117°/20 mm. (*phenylurethane*, m. p. 126°). By the elimination of water, the carbinol yields a *hydrocarbon*, $C_{11}H_{20}$, b. p. 186·5—187 5°, D^{20} 0·8120, n_D^{20} 1·4546. *i*-Methyl*cyclo*hexan-3-one condenses with acetone in the same manner as the active substance, yielding a *compound*, $C_{10}H_{16}O$, b. p. 214—217°, D^{21} 0 918, n_D 1·4704 (*semicarbazone*, m. p. 150—151°).

1-Methyl*cyclo*hexan-2-one and acetone, after keeping with alcoholic sodium ethoxide for four weeks, yield mesityl oxide and 1-*methyl*-Δ^1-*cyclo*hex*enyl-2-acetone*, b. p. 216—217°, D^{19} 0 936, n_D^{19} 1·4778 (*semi carbazone*, m. p. 173—174°); the latter yields by reduction by Paal's method, 1-*methylcyclohexyl-2-acetone*, b. p. 212—214°, D^{21} 0·9050, n_D^{21} 1·4546 (*semicarbazone*, m. p. 179°), from which 1-*methylcyclohexyl-2-acetic acid* (*silver* salt, $C_9H_{15}O_2Ag$; *amide*, m. p. 160—161°) is obtained by oxidation by alkaline hypobromite.   C. S.

Studies in the *cyclo*Pentadiene Series. II. 5-Nitro-2:3 dibenzoyl*cyclo*pentadiene. WILLIAM J. HALE and LAMBERT THORP (*J. Amer. Chem. Soc*, 1913, 35, 68—75).—It has been shown by Hale (A., 1912, i, 566) that acetonylacetone condenses with nitromalonaldehyde to form 5-nitro-2 : 3-diacetyl*cyclo*pentadiene. A similar condensation has now been effected with diphenacyl.

When diphenacyl (1 mol.) is added to a solution of sodium nitromalonaldehyde (1 mol.) and sodium hydroxide (2 mols.), and the mixture is left for eight to ten days at 40°, 5-*nitro*-2 : 3-*dibenzoyl*cyclo-*pentadiene*, $NO_2 \cdot CH \Big\langle{}^{CH:CBz}_{CH:CBz}$, m. p. 237—238° (decomp.), is obtained in a yield of 75% of that calculated from the amount of aldehyde used. The compound crystallises in yellow prisms; its *sodium*, *barium*, and *silver* salts are described. The *oxime*, m. p. 155—156° (decomp.), and the *anil*, m. p. 264—265°, form slender, yellow needles. The *phenyl-hydrazone* crystallises in yellow needles; it is unstable and readily undergoes an intramolecular condensation.

If 5-nitro-2 : 3-dibenzoyl*cyclo*pentadiene is boiled with dilute nitric acid, it undergoes oxidation with production of carbon dioxide, oxalic acid, and benzoic acid. A similar result is obtained by means of an alkaline solution of potassium permanganate, 1 mol. of the compound yielding carbon dioxide (3 mols.), oxalic acid (1 mol.), nitric acid (1 mol.), and benzoic acid (2 mols.).   E. G.

Thio-derivatives of Ketones. EMIL FROMM (*Annalen*, 1912, 394, 290—309).—[WITH FRITZ HAAS.]—The substance previously described as duplobenzylidenethioacetone by Fromm and Höller (A., 1907, i, 710) is now shown to be a mixture of stereoisomeric bases, the *duplobenzylidenethioacetoneamines*, $C_{20}H_{23}NS_2$, and its extraordinary additive compounds with acids are simply salts of these bases; consequently, the theories advanced by Fromm and Höller to explain the formation of these additive compounds are abandoned. The *hydro-chloride*, $C_{20}H_{23}NS_2,HCl$, has m. p. 238°, the *sulphate* has m. p. 192°, and the *nitrate* has m. p. 211°. The substance previously described as duplobenzylidenethioacetone hydrate, and the two additive compounds

with ammonia, m. p. 142° and 148° respectively, are simply duplo-benzylidenethioacetoneamine.

The neutral by-product, duplobenzylideneoxythioacetone, m. p. 186°, obtained by Fromm and Höller in the preparation of their so-called duplobenzylidenethioacetone (*loc. cit.*), becomes the main product when sodium sulphide is employed instead of ammonium sulphide. It is now shown to be *duplobenzylideneacetone sulphide*, $C_{20}H_{22}O_2S$. It forms a *dibromo*-derivative, $C_{20}H_{20}O_2SBr_2$, m. p. 164°, rhombic leaflets, with bromine in chloroform, and is oxidised by 5% potassium permanganate, by fuming nitric acid, or by 30% hydrogen peroxide in glacial acetic acid, to *duplobenzylideneacetone sulphoxide*, $C_{20}H_{22}O_3S$, m. p. 308°, prisms, which forms a *dibromo*-derivative, $C_{20}H_{20}O_3SBr_2$, m. p. 214°, felted needles, with bromine. By treating a not too concentrated solution of styryl methyl ketone in alcohol with ammonium poly-sulphide, *duplobenzylideneacetone disulphide*, $C_{20}H_{22}O_2S_2$, m. p. 125°, is obtained.

Since duplobenzylidenethioacetoneamine yields hydrogen sulphide, ammonia, and styryl methyl ketone-phenylhydrazone by treatment with phenylhydrazine at a temperature not exceeding 140—150°, it probably has the formula $NH[OMe(SH)\cdot CH\colon CHPh]_2$, despite its insolubility in alkalis. Moreover, since it yields duplobenzylidene-acetone disulphide by oxidation by hydrogen peroxide or by iodine, the disulphide probably has the formula $S_2[CMe(OH)\cdot CH\colon CHPh]_2$. By moistening with a little alcohol and then shaking with dilute sodium hydroxide, the disulphide is converted into the sulphide. The latter, therefore, is probably $S[CMe(OH)\cdot CH\colon CHPh]_2$, and the sulphoxide is $SO[OMe(OH)\cdot CH\colon CHPh]_2$. The disulphide and the sulphide cannot be benzoylated or acetylated, but both, and also the sulphoxide, yield styryl methyl ketone-phenylhydrazone by treatment with phenylhydrazine.

[With Emil Hubert.]—*Benzylideneacetophenone hydrosulphide*, $CHPh\colon CH\cdot CPh(OH)\cdot SH$, m. p. 107°, is obtained by the action at 0° of hydrogen sulphide on an alcoholic solution of phenyl styryl ketone containing a little potassium hydroxide. It forms a S-*benzoyl* deriv-ative, $CHPh\colon CH\cdot CPh(OH)\cdot SBz$, m. p. 125°, which is not oxidised to a disulphide by iodine. *Dibenzylideneacetophenone disulphide*,

$$S_2[CPh(OH)\cdot CH\colon CHPh]_2,$$
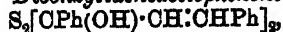
m. p. 159°, is obtained by oxidising the preceding hydrosulphide by iodine in alcohol-chloroform solution, or by adding cold alcoholic phenyl styryl ketone to alcoholic sodium sulphide saturated with sulphur and with hydrogen sulphide.

The amorphous α- and β-duplobenzylideneacetophenone sulphides, m. p. 96° and 181° respectively, described by Fromm and Lambrecht (A., 1908, i, 989), are not pure. The pure substances are crystalline, have m. p. 109° and 186° respectively, and have the formula $C_{30}H_{26}O_2S$, not $C_{30}H_{24}OS$. The views previously advanced to explain their isomerism are withdrawn. The pure substances are obtained by the action of alcoholic ammonia on phenyl styryl ketone hydrosul-phide in chloroform, an excess of ammonia producing the β-isomeride, m. p. 186°, a little ammonia forming the α-isomeride, m. p. 109°. This method of formation, together with the fact that the two sulphides

yield hydrogen sulphide and $1:3:5$-triphenylpyrazolone by boiling with phenylhydrazine in glacial acetic acid, leads to the formula $S[CPh(OH)\cdot CH:CHPh]_2$ for the two isomerides. α-Duplobenzylideneacetophenone sulphide is converted into the β-isomeride, not by iodine as stated by Fromm and Lambrecht (*loc. cit*), but by ammonia. The stereoisomerism of the two substances is probably similar to that of dioximes, consequently *cis-*, *trans-*, and *amphi*-modifications
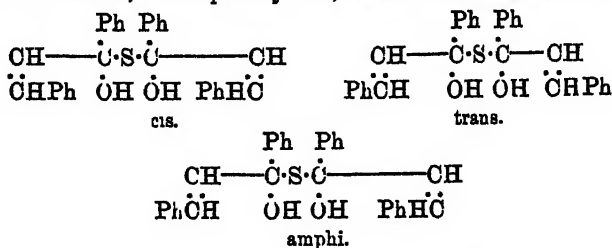
should exist.   This view of the stereoisomerism receives strong support by the discovery of the third modification required by the theory. α-Duplobenzylideneacetophenone sulphide, m. p. 109° (sulphone, m. p. 198°), is obtained by passing hydrogen sulphide, without cooling, into an alcoholic solution of phenyl styryl ketone containing a little potassium hydroxide.   β-Duplobenzylideneacetophenone sulphide, m. p. 186° (sulphone, m. p. 216°), is prepared by saturating an alcoholic solution of phenyl styryl ketone with ammonia and then with hydrogen sulphide.   γ *Duplobenzylideneacetophenone sulphide*, m. p. 212° (*sulphone*, $C_{30}H_{26}O_4S$, m. p. 276°), is obtained by adding an alcoholic solution of phenyl styryl ketone to alcohol saturated with anhydrous sodium sulphide and with sulphur.   C. S.

Stereoisomerism of Derivatives of Phenacyl Sulphide. EMIL FROMM and JULIUS FLASCHEN (*Annalen*, 1912, **394**, 310—324).— Phenacyl sulphide is obtained in almost quantitative yield by Tafel and Mauritz's method (A., 1891, 302) when the solution is kept at 0° during the reaction.   In addition to the diphenylhydrazone described by these authors, a *phenylhydrazone*, $C_{22}H_{20}ON_2S$, m. p. 126°, yellow needles, can be prepared.   Phenacyl sulphide in glacial acetic acid is oxidised to *diphenacyl sulphoxide*, $SO(CH_2\cdot COPh)_2$, m. p. 98°, and in benzene is oxidised by a faintly acidified solution of potassium permanganate to *diphenacylsulphone*, m. p. 120°, colourless prisms.   The sulphone yields *diphenacylsulphone dibenzylmercaptole*, $SO_2[CH_2\cdot CPh(S\cdot C_7H_7)_2]_2$, m. p. 110°, by treatment with an excess of benzyl mercaptan in glacial acetic acid saturated with hydrogen chloride, and forms only a *dimethyl* derivative, $SO_2(CHMe\cdot COPh)_2$, m. p. 178°, with methyl iodide and sodium ethoxide in alcohol.   In boiling glacial acetic acid, phenacylsulphone and the calculated quantity of phenylhydrazine yield *diphenacylsulphonediphenylhydrazone*,
$$SO_2(CH_2\cdot CPh:N\cdot NHPh)_2.$$
This crystallises from glacial acetic acid in yellow needles, m. p. 148°, and from alcohol or from benzene and petroleum in pale yellow needles, m. p. 160°.   This second modification, which can also be obtained by
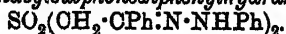
the interaction of diphenacylsulphone and phenylhydrazine in alcohol containing a little sodium hydroxide, is converted into the first modification, m. p. 148°, by crystallisation from glacial acetic acid. A third *isomeride*, m. p. 170°, is obtained from diphenacylsulphone and phenylhydrazine in alcohol, *anhydrodiphenacylsulphonephenylhydrazone*,

$$C_{22}H_{18}O_2N_2S,$$
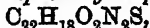
m. p. 187°, being also produced. *Diphenacylsulphonephenylhydrazone*, m. p. 193°, yellow needles, is prepared by crystallising the preceding anhydride from glacial acetic acid or by boiling equal molecular quantities of diphenacylsulphone and phenylhydrazine in the same solvent. Reasons are given for regarding this phenylhydrazone as *trans*-diphenacylsulphonephenylhydrazone and the anhydride as a derivative of the *cis*-isomeride; the diphenylhydrazones, m. p. 148°, 160°, and 170°, are regarded as having the *trans*-, *amphi*-, and *cis*-configurations respectively.

Anhydrodiphenacylsulphonedioxime,

$$\begin{matrix} CPh \cdot CH_2 \\ N\text{------}O \end{matrix} \!\!>\!\! SO \cdot CH_2 \cdot CPh \!:\! NOH,$$
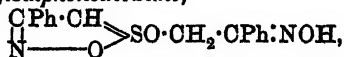
m. p. 167° white needles, prepared from diphenacylsulphone and hydroxylamine hydrochloride (2 mols.) in alcohol in the presence of sodium carbonate or acetate, yields *acetyldiphenacylsulphoneoxime*, $C_{18}H_{17}O_5NS$, m. p. 110°, by boiling with acetic anhydride. cis-*Diphenacylsulphonedioxime*, m. p. 204° (*acetyl* derivative, m. p. 158°), is obtained from diphenacylsulphone and an excess of hydroxylamine hydrochloride in boiling alcohol containing a drop of hydrochloric acid. trans-*Diphenacylsulphonedioxime*, m. p. 190° (*acetyl* derivative, m. p. 146°), is obtained together with the monoxime, m. p. 173°, by heating diphenacyl sulphone with hydroxylamine hydrochloride (2 mols.) and calcium carbonate (1 mol.) in alcohol through which carbon dioxide is being passed. cis-*Diphenacylsulphoneoxime*, $C_{16}H_{15}O_4NS$, m. p. 144°, is obtained from equal molecular quantities of diphenacylsulphone and hydroxylamine hydrochloride in the presence of sodium carbonate or acetate. trans-*Diphenacylsulphoneoxime*, m. p. 173°, is obtained from equal molecular quantities of diphenacylsulphone and hydroxylamine hydrochloride in boiling alcohol in the presence of calcium carbonate. The monoximes each yield the same acetyl derivative, m. p. 110°, as that obtained from anhydrodiphenacylsulphonedioxime. The *cis*-oxime, m. p. 144°, yields anhydrodiphenacylsulphonedioxime by further treatment with hydroxylamine hydrochloride and sodium carbonate, and the *cis*-dioxime by treatment with hydroxylamine hydrochloride and calcium carbonate. The *trans*-oxime, m. p. 173°, yields only anhydrodiphenacylsulphonedioxime by treatment with hydroxylamine hydrochloride and sodium carbonate or calcium carbonate. Since the anhydrodioxime is produced from each of the monoximes, it is certainly derived from the *amphi*-dioxime. The configurations of the other substances are not established with certainty, C. S.

Transformations of Thujane. II. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1759—1762. Compare A., 1911, i, 71, 996).—Decomposition by means of aniline or alcoholic potassium hydroxide of the unstable bromide obtained by shaking thujane with

fuming hydrobromic acid for a comparatively short time (two to three hours) yields a mixture of two isomeric hydrocarbons, $C_{10}H_{18}$, the one with the higher boiling point predominating when alkali is employed The properties of various preparations of these hydrocarbons are as follows : (1) b. p. 160—161·5°/753 mm., D_0^{20} 0 8085 (or 0·8082), n_D 1·4490, $[a]_D$ +17 86° (or +15·59°); (2) b. p 166—168°/754 mm., D_0^{20} 0·8159 (or 0·8188), n_D 1·4538, $[a]_D$ +6·13° (or +2·8°). If the action of the hydrobromic acid on thujane is prolonged for fifteen hours, distillation of the bromide yielded with aniline gives hydrocarbons with the constants : (1) b. p. 160—162°/762 mm., D_0^{20} 0 8093, n_D 1·4494, $[a]_D$ +3·67°, (2) b. p. 167 5—170°/761 mm, D_0^{20} 0 8171, n_D 1·4555, $[a]_D$ +2·4°.

Both hydrocarbons contain the same carbon atom nucleus, since reduction of them by Sabatier's method leads to one and the same hydrocarbon, $C_{10}H_{20}$, b. p. 161—163°/753 mm. (or 759 mm.), D_0^{20} 0 7904 (or 0·7902), n_D 1·4319 (or 1·4336), $[a]_D$ −1·29° (or −1·21°)

T. H. P.

A Special Case of Racemism. MAURIZIO PADOA and G. ROTONDI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 626—631).—The paper deals with the thermal analysis of the system formed by the two modifications (namely, the stable, m. p. 75°, and the labile, m. p. 45°) of optically active bromocamphor (*d*- or *l*-) This presents a case not considered by Roozeboom in his analysis of the criteria for the characterisation of inactive mixtures, because each enantiomorph exists in two modifications. Mixtures containing more than about 58% of *d*-bromocamphor, or more than 58% of *l*-bromocamphor, have an initial m. p., with separation of pure solvent. As the cooling is continued the composition mentioned is reached and the labile form then appears. At this point the whole mass solidifies and pure solvent separates along a curve shown until the inactive conglomerate is reached, which possesses the lowest transformation point. Below the curve just mentioned and the m.-p. curve of the labile modification, only conglomerates of the two bromocamphors are stable. Fused mixtures which contain less than 58% of *d*-bromocamphor and less than 58% of *l*-bromocamphor crystallise in the labile form, and when cooling is continued they are transformed into conglomerates. The labile forms have therefore a small area of stability, bounded by the curve of the labile modification and the curve of the separation of conglomerates already mentioned.

As regards the characterisation of the racemism, the racemic compound exists between 44° and 50·5°; below that it is split into inactive conglomerates. This is analogous to the behaviour of sodium ammonium racemate studied by van't Hoff.   R. V. S.

The Constituents of Essential Oils (The Constitution of Selinene). FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber*, 1912, 45, 3725—3731. Compare this vol., i, 66).—In the former communication, the sesquiterpene, selinene, was shown to give a dihydrochloride from which a regenerated selinene with slightly higher rotation, due perhaps to a different arrangement of the unsaturated linkings, could be obtained. In order to elucidate the constitution of these isomerides, they have been oxidised with ozone.

Natural ψ-(β)-selinene on oxidation gave a very small amount of an acid, but chiefly an indifferent product which was purified by conversion into a *disemicarbazone*, $C_{18}H_{20}(N \cdot NH \cdot CO \cdot NH_2)_2$, m. p. 228°, from which the saturated *diketone*, $C_{18}H_{20}O_2$, b. p. 178—180°/11 mm., D^{20} 1·0566, n_D 1·49994, $a_D + 15°$, was recovered by means of oxalic acid. The fact that two carbon atoms have been eliminated by this process, whereas the acid resulting from the oxidation by hypobromite contains only one carbon atom less, indicates the presence in selinene of one methylene group attached directly to the ring and another in a side-chain.

Regenerated selinene, *ortho*-(a)-selinene, b. p. 128—132°/11 mm., D^{20} 0·9190, n_D 1·50920, $a_D + 61°36'$, gives much less of the diketone on treatment with ozone, the chief product being the acid, which has been characterised as *methyl selinenediketomonocarboxylate*, $C_{15}H_{24}O_4$, b. p. 185—190°/11 mm., D^{20} 1·0635, n_D 1·47889, $a_D + 4°24'$. The formation of this acid is explained by assuming that the elimination of hydrogen chloride from the dichloride has resulted in the displacement of a double bond into the ring. A consideration of other sesqui-terpenes leads to the adoption of the annexed formulæ.
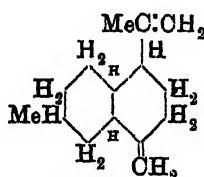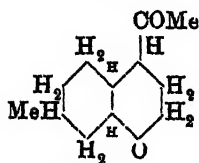
ψ-(β)-Selinene.

$\downarrow$ Ozone

Diketone.
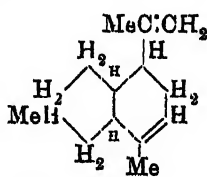
Ortho-(a)-selinene.

$\downarrow$ Ozone
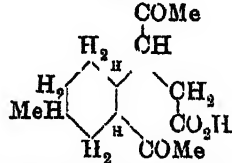
Diketomonocarboxylic acid.

J. C. W.

Chemical Investigation of the Oil of Chenopodium. II. E. K. NELSON (*J. Amer. Chem. Soc.*, 1913, **35**, 84—90. Compare A., 1911, i, 797).—It has been found that when the glycol anhydride formed by the molecular rearrangement of ascaridole is treated with dilute sulphuric acid, ascaridole α-glycol is produced together with two other crystalline substances, one of which, termed *ascaridole β-glycol*, $C_{10}H_{18}O_3$, crystallises with $1H_2O$; the anhydrous substance has m. p. 103—105°; when this glycol is warmed with dilute sulphuric acid, thymol is produced. The other *substance*, termed the "erythrite," $C_{10}H_{20}O_4$, also crystallises with $1H_2O$, and when anhydrous has m. p. 128—130°; it is decomposed by boiling dilute sulphuric acid with formation of a *ketone*, with a strong menthone-like odour, and a

phenolic substance, m. p. 80—81°; the *semicarbazone* of the ketone has m. p. 182—184°. On oxidising the "erythrite" with alkaline potassium permanganate, an *acid*, $C_{10}H_{18}O_6$, m. p. 190—191°, is produced, which forms rhombic prisms; when this acid is heated at 210°, it is converted into its anhydride, and on further heating yields ascaridic anhydride, m. p. 70—71°. If the acid $C_{10}H_{18}O_6$ is oxidised with potassium permanganate in presence of sulphuric acid, it yields β-methylheptane-$\gamma\zeta$-dione, and it is therefore probable that it is a modification of $\alpha\alpha$-dihydroxy-α-methyl-α-*iso*propyladipic acid. The "erythrite" therefore probably has the structure

$$OH \cdot CMe \overset{CH_2 \underline{\hspace{1cm}} CH_2}{\underset{CH(OH) \cdot CH(OH)}{\big<}} C(C_3H_7) \cdot OH.$$
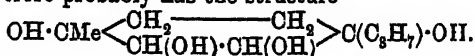
The acid, $C_{10}H_{16}O_5$, obtained by the oxidation of the α-glycol, is converted by further oxidation into β-methylheptane-$\gamma\zeta$-dione. When the glycol anhydride is boiled with a saturated solution of oxalic acid, a small quantity of the phenolic substance, m. p. 80—81°, is produced, which is formed on boiling the "erythrite" with dilute sulphuric acid and is also obtained by treating the α-glycol with strong dehydrating agents. On heating the glycol anhydride with benzoic anhydride at 150°, an ester of carvacrol is produced.

From the results of this work, it is considered that the α-glycol has the constitution $CMe \overset{CH_2 \underline{\hspace{1cm}} CH_2}{\underset{CH(OH) \cdot CH(OH)}{\big<}} \overset{\big\backslash}{\underset{\big/}{O}} C \cdot C_3H_7$, and that the acid obtained by its oxidation has the structure of $\alpha\delta$-cineolic acid, $CO_2H \cdot CMe \cdot CH_2 \cdot CH_2 \cdot C(C_3H_7) \cdot CO_2H$.   E. G.

Action of Gaseous Oxygen on Caoutchouc STANLEY J. PEACHEY (*J. Soc. Chem. Ind.*, 1912, 31, 1103—1104).—When purified caoutchouc, in the form of a thin film, is exposed to an atmosphere of oxygen at a temperature of 85°, oxidation commences after a few hours' heating, and then proceeds rapidly to completion. Results of experiments with Ceylon caoutchouc show that, under these conditions, each $C_{10}H_{16}$ unit of the molecule combines with 4 atoms of oxygen. This result is not in agreement with that obtained by Herbst (A., 1906, 1, 196), and it may be assumed that the reaction which takes place when caoutchouc in benzene solution is oxidised by air (as in Herbst's experiments) differs from that which occurs when caoutchouc itself is oxidised by pure oxygen. The oxidation most probably results in the formation of additive products.   W. P. S.

The Nitrogenous Constituent of Para Caoutchouc and Its Bearing on the Nature of Synthetic Caoutchouc. CLAYTON BEADLE and HENRY P. STEVENS (*J. Soc. Chem. Ind.*, 1912, 31, 1099—1101. Compare A., 1912, i, 789).—It is shown that the removal of insoluble (nitrogenous) constituents from caoutchouc results in deterioration of the latter, although it is open to question how far the quality of caoutchouc is improved by the presence of more than a certain proportion of insoluble matter. In the vulcanisation process the insoluble matter appears to play the part of a sulphur carrier.

The authors have also made experiments on the influence of the resinous constituents on the vulcanising properties of caoutchouc, and find that the removal of the resins results in a marked deterioration of the quality of the caoutchouc. The absence of nitrogenous substances and resins in synthetic caoutchouc should make the latter inferior to natural rubber. W. P. S.

Chemistry of Caoutchouc. VI. Theory of Vulcanisation. IV. DAVID SPENCER and C. A. WARD (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 274—280. Compare A., 1912, i, 706).—Experiments have been made to ascertain whether the so-called "depolymerisation" of caoutchouc, which is brought about by mechanical or thermal treatment, is accompanied by a change in the rate at which it reacts with sulphur in the process of vulcanisation. For this purpose comparative measurements were made with two exactly similar mixtures of 100 parts of caoutchouc and 10 parts of sulphur. In the one case the caoutchouc was kneaded for thirty minutes at a moderate temperature, the sulphur being then added, and the mixing effected by a further kneading for ten minutes. In the second case, the treatment was similar, except that the caoutchouc was subjected to the mechanical treatment for ninety minutes at a much higher temperature.

From the observations made on the rate of vulcanisation at 135°, it appears that there is no appreciable difference between the two samples, and the authors draw the conclusion that "depolymerisation" has no influence whatever on the chemical result of the vulcanisation process. The conclusions arrived at by Axelrod (*Gummi Zeit.*, 1909, 24, 352) are therefore not confirmed by these experiments. H. M. D.

The Action of Chloroacetyl Chloride on Ethyl Malonate; Iminotetronic Acid. ERICH BENARY (*Ber.*, 1912, 45, 3682—3686). —As the substance described as the ester-amide of tetramic acid (Benary, A., 1911, i, 672) is in reality ethyl iminotetron-α-carboxylate (Anschütz, A., 1912, i, 836), the compound $C_9H_{12}O_5$, from which it is obtained by the action of ammonia, is presumably ethyl *iso*tetron-α-carboxylate; this view is supported by the action of organic bases which give compounds similar to that produced by ammonia; these compounds are probably ketonic, but do not yield phenylhydrazones (compare Wolff, A., 1900, i, 582); they frequently yield salts, however, derived from the enolic structure.

Ethyl phenyliminotetron-α-carboxylate, $\begin{matrix} CH_2—CO \\ O\cdot C(:NPh) \end{matrix}\!\!>\!CH\cdot CO_2Et$, obtained by the interaction of equivalent quantities of ethyl *iso*tetron-α-carboxylate and aniline, crystallises in needles, m. p. 116—117°; it exhibits both acidic and basic properties.

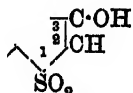Ethyl phenylhydrazinotetron-α-carboxylate (already described) yields a *potassium* salt.

Ethyl piperidinoisotetron-α-carboxylate, $\begin{matrix} CH_2—CO \\ O\cdot C(C_5NH_{10}) \end{matrix}\!\!>\!C\cdot CO_2Et$, m. p. 107.—108°, from equal weights of piperidine and ethyl *iso*tetron-

α-carboxylate, as might be expected from the structure, has no acidic properties.

When iminotetronic acid in benzene solution is treated with rather more than an equimolecular quantity of bromine, *bromoiminotetronic acid*, $\begin{smallmatrix} CH_2 \cdot C(OH) \\ O—C(:NH) \end{smallmatrix}\!\!>\!CBr$, needles, m. p. 182°, is obtained; it gives a red coloration with ferric chloride.

On adding ice to the reaction mixture from iminotetronic acid and nitric acid, aci-*nitroiminotetronic acid*, $\begin{smallmatrix} CH_2—CO \\ O \cdot C(:NH) \end{smallmatrix}\!\!>\!C:NO_2H$, is precipitated, leaflets, m. p. 255—258° (decomp.); it is a strongly acidic substance, which gives a *phenylhydrazone*, yellow tablets, m. p. 211—212°.

The conclusion is drawn that the action of chloroacetyl chloride on ethyl sodiomalonate consists of two concurrent processes, one of which produces unstable ethyl chloroacetylmalonate, which undergoes spontaneous change into ethyl tetron-α-carboxylate, whilst the other process involves the enolic form of ethyl sodiomalonate, which reacts with the acid chloride producing ethyl *iso*tetron-α-carboxylate.   D. F. T.

Hydroxymethylfurfuraldehyde. FRANCESCO ANGELICO and A. COPPOLA (*Gazzetta*, 1912, **42**, ii, 583—589).—The authors confirm the formula for this substance given by Fenton and Gostling (T., 1889, **75**, 423), and by the application of the Angeli-Rimini reaction they have prepared from it *α-hydroxymethylfuranhydroxamic acid*, $C_6H_7O_4N$, which crystallises in pink, lustrous, soapy scales, m. p. 139°, the free acid being prepared from the *copper salt*, $(C_6H_6O_4N)_2Cu,H_2O$. When the acid is hydrolysed with 25% sulphuric acid, it yields hydroxylamine and hydroxypyromucic acid (m. p. 165°).
     R. V. S.

Constitution of Bergapten. HERMANN THOMS and E. BAETCKE (*Ber.*, 1912, **45**, 3705—3712).—Bergapten, which Pomeranz showed to be a coumarin-coumarone derivative of phloroglucinol (A., 1892, 71; 1893, 342), was found to occur in certain fruits accompanied by an isomeride, xanthotoxin (A., 1912, i, 40), to which the formula (I) was assigned. Bergapten has now been converted into an amine, and this into a quinone containing no methoxy-group, from which the conclusion is drawn that the methoxy-group is *para* to the unsubstituted carbon atom, and that the substance has the constitution (II).

I. $CH\!\!<\!\!\begin{smallmatrix} O \\ CH \end{smallmatrix}\!\!>\!\!\begin{smallmatrix} OMe \\ O—CO \\ CH:CH \end{smallmatrix}$ II. $CH\!\!<\!\!\begin{smallmatrix} CH \\ O \end{smallmatrix}\!\!>\!\!\begin{smallmatrix} OMe \\ CH:CH \\ O—CO \end{smallmatrix}$

This is confirmed by the fact that xanthotoxin yields the same quinone.

Aminobergapten, $C_{12}H_7O_4 \cdot NH_2$, is obtained by the reduction of the nitro-derivative (Pomeranz, *loc. cit.*) with tin and hydrochloric acid, in slender, pale yellowish-green needles, m. p. 198°, and yields an *acetyl* compound, m. p. 208°. When oxidised with sodium dichromate the

methoxy-group is replaced, and the golden-yellow *quinone*, $C_{11}H_4O_5$, m. p. 248—250°, is formed. *Aminoxanthotoxin* is prepared in the same way, and is similar in appearance to its isomeride; it melts, however, at 236°, is more easily acetylated, yielding an *acetyl* compound, m. p. 246—247°, and is much less soluble in cold sulphuric acid, but it yields the same quinone.

The *quinol*, $C_{11}H_4O_3(OH)_2$, crystallises with $2H_2O$ in light green needles, which lose water at 110°, and yield a *diacetyl* compound, m. p. 208—209°, and a *diphenylurethane* derivative, $C_{11}H_4O_3(O \cdot CO \cdot NPh_2)_2$, m. p. 229—230°.

<div align="right">J. C. W.</div>

Action of Hydrogen Peroxide on Hydroxythionaphthen, Hydroxythionaphthen Carboxylic Acid, and "Thioindigo."

MAURICE LANFRY (*Compt. rend.*, 1912, 155, 1517—1519. Compare A., 1912, i, 293).—Hydroxythionaphthen in alkaline solution gives a blue precipitate on the addition of hydrogen peroxide, leaving a brown liquid, from which only gummy substances could be extracted. The blue precipitate on solution in water and addition of strong acid gives a red, flocculent precipitate, which resembles "thioindigo" in all its properties. The addition of hydrogen peroxide to a boiling solution of hydroxythionaphthen in acetic acid gives a red precipitate of "thioindigo," which slowly dissolves and the solution becomes colourless. Extraction with benzene separates out 3-*hydroxy*-1-*dioxythionaphthen* (annexed constitution), m. p. 139°, which in its chemical properties closely resembles the hydroxythionaphthen from which it is prepared.

The effect of hydrogen peroxide on the sodium salt of hydroxythionaphthencarboxylic acid is to destroy its phenolic character with the formation of a small quantity of "thioindigo." The major part of the salt is resinified.

In the presence of hydrogen peroxide, finely divided "thioindigo" slowly dissolves in acetic acid to a red solution, which gradually becomes decolorised. The only products of extraction were gummy substances.

<div align="right">W. G.</div>

"Bisphenylthiophenindigo" [5 : 5′- Diphenyl-$\Delta^{2,2'}$-bisthiophen-3-one]. PAUL FRIEDLAENDER and ST KIELBASINSKI (*Ber.*, 1912, 45, 3389—3396).—Although *m*-hydroxydiphenyl shows no tendency to pass over into an ortho-quinonoid compound, the analogous 3-hydroxy-5-phenylthiophen behaves entirely differently, readily forming "*bisphenylthiophenindigo*,"

The dye is prepared by the following series of operations. On heating ethyl cinnamate with sulphur, a disulphide, thiobenzoylthioacetic acid, $S\diagdown\substack{S—CO \\ CPh:CH}$ (Baumann and Fromm, A., 1897, i, 191), is formed. The ring is opened by sodium sulphide, and by the action of chloroacetic acid a compound,

$$CO_2H \cdot CH_2 \cdot S \cdot CPh:CH \cdot CO \cdot S \cdot CH_2 \cdot CO_2H,$$

is formed, which when boiled with acetic anhydride is converted into acetoxyphenylthiophen, $S<^{CH-C \cdot O \cdot CO \cdot CH_3}_{CPh:CH}$. On hydrolysis, 4-hydroxy-2-phenylthiophen is obtained.

This condenses with aromatic aldehydes or with isatin to dyes, forms a quinoneoxime with nitrous acid, and is converted by alkaline or acid oxidising agents into " bisphenylthiophenindigo."

The *disulphide* crystallises in broad needles, m. p. 156°.

4-Hydroxy-2-phenylthiophen separates in slender needles, m. p. 78°, the *acetyl* derivative forms broad, colourless, compact platelets, m. p. 75°.

The *quinone oxime*, $S<^{CPh \!=\!=\! CH}_{C(:N \cdot OH) \cdot CO}$, prepared by interaction with sodium nitrite, forms broad faint. brownish-yellow needles, m. p. 216°.

On bromination, a *product*, $CPh<^{CBr \cdot CO}_{S-CBr_2}$, is obtained, crystallising in brownish-yellow plates, m. p. 134°. It does not react simply with aniline : on warming with sodium acetate, slender, red needles or ruby-red prisms of a brominated diphenylthiophenindigo are obtained.

4-Hydroxy-2-phenylthiophen reacts with piperonal, the *condensation* product crystallising in long, yellow needles, m. p. 196°.

"*Bis-5-phenyl-2-thiophenindigo*" [5 . 5'-diphenyl-Δ²⁻²'-bisthiophen 3-one] separates in brownish-red, lustrous needles, m. p. 280°.

" *5-Phenyl-2-thiophen-3 indoleindigo* " [5-phenyl-2-(3'-indoxyl)-thiophen-3-one], produced on condensation with isatin, crystallises in sealing wax-red needles, m. p. 281°.

" *5-Phenyl-2-thiophen-2-indoleindigo* " [5-phenyl-2-(2'-indoxyl)-thiophen-3-one], $^{CH \cdot CO}_{CPh \cdot S}>C:C<^{CO}_{NH}>C_6H_4$, obtained on boiling isatin-anilide with phenylhydroxythiophen in acetic anhydride, crystallises in slender, dark violet needles.   E. F. A.

Methylation of Histidine, Arginine, and Lysine. I. R. ENGELAND and FRIEDRICH KUTSCHER (*Zeitsch. Biol* , 1912, 59, 415—419). —On methylation of histidine monochloride with methyl sulphate and barium hydroxide, *pentamethylhistidine* is obtained. The *aurichloride* crystallises in large, lustrous needles, the *chloride* is an oil, and the free base decomposes rapidly. Small quantities of the crystalline *aurichloride* of tetramethylhistidine are obtained at the same time.

Under similar conditions, arginine yields a *tetramethyl* derivative, the *aurichloride* forms short, stout needles, m. p. 173—175°. Three of the methyl groups are attached to nitrogen in the side-chain, one only to nitrogen in the guanidine complex.

Lysine yields a compound, probably the *ethyl* ester of *hexamethyllysine*, which gives an *aurichloride*, m. p. 208°, corresponding with the formula $C_{14}H_{34}O_3N_2,Au_2Cl_8$.   E. F. A.

Strychnos Alkaloids. XVI. **Dihydrobrucinoic Acid and** *iso*Brucinolone. HERMANN LEUCHS and GEORGE PEIRCE (*Ber.*, 1912, 45, 3412—3420).—Dihydrobrucinonic acid, which contains an alcoholic

hydroxyl (compare A.. 1212, i, 210), forms an acetyl derivative when acted on by acetic anhydride and sodium acetate. More vigorous action produces a neutral compound containing two further acetyl residues less a molecule of water. Dihydrobrucinonic acid does not react with nascent hydrogen or with hydroxylamine. It is broken down by sodium hydroxide into glycollic acid and *iso*brucinolone, $C_{21}H_{22}O_7N_2$. The latter forms an acetyl derivative, and on treatment with concentrated hydrogen chloride gives iso*brucinolone hydrate*. At higher temperatures this is reconverted into *iso*brucinolone (compare Leuchs and Brewster, A., 1912, i, 210). With concentrated nitric acid a nitro-derivative, $C_{19}H_{15}O_7N_3$, is obtained; the change involves the formation of a quinone and the subsequent nitration of this. With sulphurous acid a paler reduction compound is obtained from the quinone.

Acetyldihydrobrucinonic acid forms colourless, four-sided prisms, m. p. 235—238°. The neutral product, $C_{27}H_{28}O_9N_2$ or $C_{29}H_{30}O_{10}N_2$, crystallises in colourless, chisel-shaped prisms, m. p. 280—282°, after becoming yellow at 260°.

By the action of acetic anhydride on brucinonic acid, a compound,

$$(C_{18}H_{14}O_4N)_x$$

is obtained, crystallising in long, matted, lustrous needles, m. p. 125—127°.

*Acetyliso*brucinolone forms large, colourless platelets, m. p. 281—283° (decomp.).

iso*Brucinolone hydrate* separates in four-sided prisms, which froth at 205—208°, become solid again, turn brown at 290°, m. p. 310—315° (decomp.).

The *hydrochloride* forms four-sided platelets; the *sulphate* consists of massive prisms, which become brown at 235°, decomp. 238°.

*Nitrobisapomethyldihydroiso*brucinolone crystallises in flat, orange-yellow needles, which become brown at 250°, and completely charred at 340°.

*Nitrobisapomethyliso*brucinolone gives massive, reddish-yellow prisms, which become brown at 240°.

Nitrobisapomethylbrucinolone crystallises in small, yellow octahedra, dissolving in concentrated sulphuric acid with a yellow coloration and in concentrated sodium hydroxide with a violet coloration.

E. F. A.

Strychnos Alkaloids. XVII. Isolation of the Hydrate of a Fourth Strychninesulphonic Acid. HERMANN LEUCHS and JOHANNES WUTKE (*Ber*, 1912, 45, 3686—3691).—Analogous to the fourth brucinesulphonic acid (Leuchs and Geiger, A., 1911, i, 1018), a fourth strychninesulphonic acid (compare Leuchs and Schneider, A., 1909, i, 671) has been obtained as a very stable hydrate, which retains the additional water very tenaciously.

The solution of the reaction product obtained as described earlier (Leuchs and Schneider, *loc. cit.*), after crystallisation of strychnine-sulphonic acids I and II, and subsequent concentration under reduced pressure, deposits a mixture of the acids I, II, and III with the above-mentioned hydrate, which last can be separated in the free

state and also as a compound with strychninesulphonic acid III; the total yield of hydrate in the two forms amounts to approximately 3%.

Strychninesulphonic acid IV *hydrate*, $C_{21}H_{24}O_6N_2S,2H_2O$, stout prisms or rhombohedra, m. p. 275° (decomp.), $[a]_D^{20} + 18\cdot3°$, could not be dehydrated beyond $C_{21}H_{24}O_6N_2S$, even at 135° in a vacuum over phosphoric oxide. The *double* compound with strychninesulphonic acid III, $C_{21}H_{22}O_5N_2S,C_{21}H_{24}O_6N_2S$, slender prisms or needles, m. p. 250° (decomp.), $[a]_D^{20} + 101°$, can also be obtained by mixing solutions of the hydrate and excess of the acid III; in the absence of excess of strychninesulphonic acid III, the compound is resolved by hot water into its constituents.   D. F. T.

Synthesis of **Hæmopyrrole-*b***. OSKAR PILOTY and A. BLOMER (*Ber.*, 1912, **45**, 3749—3753).—Ethyl acetylpyruvate condenses with aminobutanone or with aminoacetone to form pyrrole derivatives. In the former case, 4-acetyl-2 : 3-dimethylpyrrole-5-carboxylic acid,

$$NH\!<\!\genfrac{}{}{0pt}{}{C(CO_2H)\!:\!C\cdot COMe}{CMe\!=\!=\!CMe}\;,$$
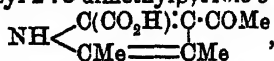
is obtained, which on heating at 215° is converted into 4-*acetyl*-2 : 3-*dimethylpyrrole*, $NH\!<\!\genfrac{}{}{0pt}{}{CH\!=\!C\cdot COMe}{CMe\!:\!CMe}$. When this is treated with hydrazine and sodium ethoxide, 2 : 3-dimethyl-4-ethylpyrrole (hæmo-pyrrole-*b*), $NH\!<\!\genfrac{}{}{0pt}{}{CH\!=\!CEt}{CMe\!:\!CMe}$, is formed.

With aminoacetone the product is 4-*acetyl-3-methylpyrrole-5-carb-oxylic acid*, $NH\!<\!\genfrac{}{}{0pt}{}{C(CO_2H)\!:\!C\cdot COMe}{CH\!=\!=\!CMe}$. This has m. p. 200°. During the reaction an isomeric by-product, m. p. 250° (decomp.), is also formed.

4-*Acetyl*-2 : 3-*dimethylpyrrole-5-carboxylic acid* crystallises in colour-less, prismatic rods, m. p. 204° (decomp.).

4-*Acetyl*-2 : 3-*dimethylpyrrole* separates in short, colourless, prismatic platelets with sharp edges, m. p. 137°. The synthetic hæmopyrrole-*b* is identical with the natural compound.   E. F. A.

Cyclic Imines. VII. Ahrens' So-called γ-Picoline. JULIUS VON BRAUN and A. SCHMATLOCH (*Ber.*, 1912, **45**, 3649—3652).—The method described by Ahrens for the separation of pure 4-methylpyridine (γ-picoline) by precipitation with mercuric chloride (A., 1905, i, 232) is found to yield a mixture instead of a pure product.

Successive reduction and benzoylation of 4-methylpyridine, prepared by Ahrens' method, produced a *benzoyl* derivative, $C_6H_{12}NBz$, b. p 189—190°/17 mm., which on distillation with phosphorus pentabromide (compare von Braun and Sobecki, A., 1911, i, 413) formed a product which could be separated into two fractions by distillation. The smaller and less volatile portion, b. p. 150°/19 mm., $D_4^{20} 1\cdot9305$, was probably *aβε-tribromo-β-methylpentane*, and gave an unsaturated organo magnesium compound which absorbed carbon dioxide with the formation of *δ-methylene-n-hexoic acid*, $CO_2H\cdot[CH_2]_3\cdot CMe\!:\!CH_2$, b. p. 218—221°, $D_4^{20} 0\cdot9406$, $n_D 1\cdot4442$; the formation of this series of compounds is attributed to the presence of 3-methylpyridine in the

original base. The more volatile fraction, $C_6H_{12}Br_2$, b. p. 115—120°/ 19 mm., D_4^{20} 1·608, on treatment with potassium cyanide yielded a dinitrile, $C_6H_{12}(CN)_2$, b. p. 171—174°/10 mm., which was hydrolysable, apparently to a mixture of β- and γ-methylpimelic acids. Neither fraction therefore was of pure 4-methylpyridine. D. F. T.

The Action of Hydroxylamine and Phenylhydrazine on Benzoyldehydracetic Acid. A Correction. Joh. Schöttle (*Ber.*, 1912, **45**, 3779. Compare A., 1912, i, 915).—Reaction between free hydroxylamine and benzoyldehydracetic acid was effected by mixing hydroxylamine sulphate with the theoretical quantity of alcoholic potassium hydroxide, filtering the precipitated potassium sulphate, and adding the phenyl-lactam of benzoyldehydracetic acid to the filtrate.

E. F. A.

Cyclic Imines. VI. Ring Homologues of Tetrahydroquinoline. Julius von Braun and B. Bartsch (*Ber.*, 1912, **45**, 3376—3389).—The tendency to form seven-membered rings such as hexamethyleneimine is very much increased when two of the carbon atoms are members of a benzene nucleus; thus o-δ-chlorobutylaniline, on elimination of hydrogen chloride, readily forms *tetrahydrohomoquinoline*, $C_6H_4{<}{CH_2 \cdot CH_2 \atop NH-CH_2}{>}CH_2$. The constitution of the quinoline is established by the fact that when the ring is opened by the action of phosphorus pentachloride, δ-chloro-o-benzoylaminobutylbenzene, $COPh \cdot NH \cdot C_6H_4 \cdot [CH_2]_4Cl$, is formed, which is in turn convertible into the already known δ-o-benzoylaminophenylvaleric acid.

Homotetrahydroquinoline resembles the isomeric 2-methyltetrahydroquinoline and the lower ring homologues in its stability towards hydrolytic and reducing reagents, and also towards oxidation; it is hardly altered by distillation with silver sulphate.

The quinoline could not be prepared by other methods, such as the distillation of δ-o-diaminobutylbenzene hydrochloride or by the interaction of γ-phenylpropylamine with formaldehyde.

o-*Amino-δ-hydroxybutylbenzene*, $NH_2 \cdot C_6H_4 \cdot [CH_2]_4 \cdot OH$, prepared by the reduction of the ester, $NH_2 \cdot C_6H_4 \cdot [CH_2]_3 \cdot CO_2Et$, by means of sodium and alcohol, is a viscid, almost odourless oil, b. p. 180—183°/12 mm. The *dibenzoyl* compound crystallises in snow-white platelets which sinter at 127°, m. p. 130°; the *platinichloride* forms dark red platelets, which blacken at 168°, m. p. 175°; the *picrate* separates in green leaflets, m. p. 179°.

o-*Amino-δ-chlorobutylbenzene* was not obtained pure; the *platinichloride* crystallises in pale yellow platelets, m. p. 182—183°.

Tetrahydrohomoquinoline is an almost colourless oil, b. p. 131—133°/ 16 mm., 253—255°/760 mm., D_4^{20} 1·0325, solidifying to colourless crystals, m. p. 32°. The *hydrochloride* has m. p. 186°; the pale yellow, granular crystals of the *platinichloride* blacken at 192°, m. p. 194°; the *picrate* crystallises in yellowish-red needles, m. p. 179°; the *benzoyl* derivative has m. p. 96°, whilst the *benzenesulphonyl* compound has m. p. 109°.

The *platinichloride* of the *dimethyl* derivative, $C_{10}H_{12}NMe_2PtCl_6$, produced on long heating with methyl iodide, has m. p. 197°.

When heated with phosphorus pentachloride at 150°, tetrahydro-homoquinoline yields δ-*chloro*-o-*benzoylaminobutylbenzene*, which crystallises in lustrous, silvery platelets, m. p. 117°. The corresponding iodide when decomposed with potassium cyanide yields δ-*benzoyl-aminophenylvaleronitrile*, $C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot [CH_2]_4\cdot CN$, m. p. 114°, from which the corresponding acid (A., 1907, i, 524) is obtained on hydrolysis.

δ-o-*Diaminobutylbenzene*, prepared by reducing the nitrile of o-benzoylaminophenylbutyric acid, forms a colourless oil of strongly basic odour, b. p. 172°/14 mm.

o-γ-*Chloropropylbenzonitrile* is a pale yellow oil, volatile in steam, b. p. 153°/19 mm. On hydrolysis, o-γ-*chloropropylbenzoic acid*,

$$CO_2H\cdot C_6H_4\cdot [CH_2]_3\cdot Cl,$$
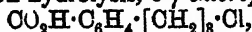
is obtained, m. p. 79°.

The nitrile condenses with sodium phenoxide to o-γ-*phenoxypropyl-benzonitrile*, $CN\cdot C_6H_4\cdot [CH_2]_3\cdot OPh$, a pale yellow oil, b. p. 210°/23 mm. The corresponding o-γ-*phenoxypropylbenzoic acid* has m. p. 120°.   E. F. A.

Thiazoles. REINHOLD VON WALTHER and H. ROCH (*J. pr. Chem.*, 1913, [ii], 87, 27—66).—Although the condensation of thiocarbamide with ω-bromoacetophenone and other halogeno-ketones of the type $CHXR\cdot COR$ may give rise to either aminothiazoles (formula II below, R' and R" = H) or iminothiazolines (IV or V, R',R" = H), the work of Traumann (A., 1889, 414) and others has shown that only amino-thiazoles are produced. s-Disubstituted thiocarbamides always yield iminothiazolines, whilst the as-disubstituted derivatives give rise to aminothiazoles.
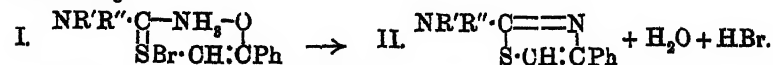
With respect to the mechanism of the condensation, the authors suggest that the first stage consists in the addition of the halogeno-ketone to the sulphur atom of the thiocarbamide, and that the removal of hydrogen haloid and water from the intermediate compound thus produced is preceded by the formation of an internal salt, derived from the enolic form, the constitution of this salt being determined by the relative basicity of the amino-residues of the thiocarbamide ; thus, in the condensation of as-disubstituted thiocarbamides,

$$NR'R''\cdot CS\cdot NH_2,$$
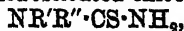
with ω-bromoacetophenone, the compound
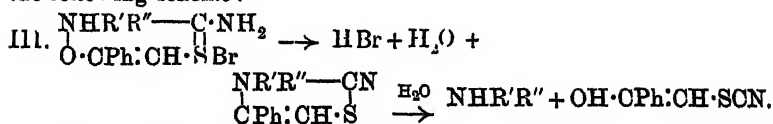
$$NR'R''\cdot C(NH_2){:}SBr\cdot CH_2\cdot COPh$$
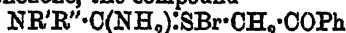
is first produced, which is transformed successively into the enolic salt I and aminothiazole II if NHR'R" is more feebly basic than NH_3 :

I. $\begin{array}{c} NR'R''\cdot C-NH_2-O \\ SBr\cdot CH{:}CPh \end{array}$ →   II. $\begin{array}{c} NR'R''\cdot C{=\!=}N \\ S\cdot CH{:}CPh \end{array}$ + H_2O + H.Br.

On the other hand, if NHR'R" is a stronger base than NH_3, the compound III is formed as an intermediate product, which decomposes

into a secondary amine and thiocyanoacetophenone as shown in the following scheme :

III. $\begin{matrix} \text{NHR'R''} & \text{—C·NH}_2 \\ \text{O·CPh:CH·S} & \text{Br} \end{matrix} \longrightarrow \text{HBr} + \text{H}_2\text{O} +$

$\begin{matrix} \text{NR'R''} & \text{—CN} \\ \text{CPh:CH·S} & \end{matrix} \xrightarrow{\text{H}_2\text{O}} \text{NHR'R''} + \text{OH·CPh:CH·SCN}.$

An explanation is thus afforded of the behaviour of *as*-dimethylthiocarbamide, which, with ω-bromoacetophenone, does not form an aminothiazole, but undergoes decomposition into dimethylamine and thiocyanoacetophenone (Spica and Carrara, A., 1892, 215).

s-Disubstituted thiocarbamides, NHR'·CO·NHR'', in which the amino-residues are of approximately equal basicity, may give rise to two isomeric iminothiazolines :

IV. $\begin{matrix} \text{CPh·NR''} \\ \text{CH——S} \end{matrix}{>}\text{C:NR'}$ V. $\begin{matrix} \text{CPh·NR'} \\ \text{CH——S} \end{matrix}{>}\text{C:NR''} ;$

the formation of isomerides of this kind has been observed by Stenz (*Diss.*, Dresden, 1899) and Wünsche (*ibid.*, 1901). When the basicity of one of the amino-groups is much greater than that of the other, only one isomeride will be formed ; thus, both *s-p*-tolylbenzylthiocarbamide and *s-p*-tolylmethylthiocarbamide condense with ω-bromoacetophenone to form only one iminothiazoline (formula V, where R''=*p*-C₆H₄Me, and R'=·CH₂Ph or Me). The constitution of the iminothiazolines derived from *s*-disubstituted thiocarbamides is readily determined (1) by heating with carbon disulphide, which leads to the removal of the imino-group as the corresponding thiocarbimide, or (2) by hydrolysis with hydrochloric acid, the imino-group, in this case, being removed in the form of a primary amine.

With respect to the thiazoles derived from mono-substituted thiocarbamides, the authors point out that no definite proof of their constitution has hitherto been brought forward. Although the work of Traumann (*loc. cit.*) appears to indicate that the thiazole obtained from methylthiocarbamide and ω-bromoacetophenone is probably a 2-methylimino-4-phenylthiazoline, the observations described in the present paper prove conclusively that the thiazole derived from *p*-tolylthiocarbamide has the constitution of an aminothiazole.

2-p-Toluidino-4-phenylthiazole, $\begin{matrix} \text{CPh·N} \\ \text{CH—S} \end{matrix}{>}\text{C·NH·C}_6\text{H}_4\text{Me}$, is obtained

in the form of its *hydrobromide*, slender needles, m. p. 205° (decomp.), by heating *p*-tolylthiocarbamide with ω-bromoacetophenone in alcoholic solution, the free base being liberated from the hydrobromide by warming with pyridine. It crystallises in leaflets, m. p. 123°, and forms a *hydrochloride*, which melts and becomes green at 212°, a *sulphate*, m. p. 152°, an *acetate*, m. p. 85°, and *thiocyanate*, m. p. 125°, all of which crystallise in colourless needles ; the *platinichloride* forms orange leaflets, m. p. 230°, the *picrate*, yellow needles, m. p. 185°. It reacts with phenylcarbimide in ethereal solution to form the *carbamide*, $\begin{matrix} \text{CPh·N} \\ \text{CH—S} \end{matrix}{>}\text{C·N(C}_6\text{H}_4\text{Me)·CO·NHPh}$, crystallising in lustrous leaflets,

m. p. 196·5°. Towards both oxidising and reducing agents the thiazole is remarkably stable, but is decomposed by hydrochloric acid at 225—250° into acetophenone, p-toluidine, and ammonia; when heated with carbon disulphide at 250°, it forms p-tolylthiocarbimide.

The *acetyl* derivative, $C_{18}H_{16}ON_2S$, forms colourless prisms, m. p. 124·5°; the *benzoyl* derivative, prepared by the pyridine method in benzene solution, crystallises in hard prisms, m. p. 207°.

With the object of synthesising the above acyl derivatives, the authors have endeavoured to condense ω-bromoacetophenone with *s*- and *as*-acetyl-p-tolylthiocarbamide and *s*-benzoyl-p-tolylthiocarbamide in alcoholic solution, but find that no condensation occurs. It would thus appear that acylthiocarbamides are incapable of undergoing the thiazole condensation.

2-p-Toluidino-4-phenylthiazole combines with 1-chloro-2:4:6-trinitrobenzene in hot alcoholic solution to form an unstable, additive *compound*, $C_{22}H_{16}O_6N_5SCl$, which crystallises in red needles, m. p. about 90°, and is resolved by acids or alkalis into its components; the additive *compound* with 1-chloro-2:4-dinitrobenzene forms stout, dark red crystals, m. p. about 60°.

as-p-*Tolylbenzylthiocarbamide*, $C_6H_4Me·N(CH_2Ph)·CS·NH_2$, obtained by heating N-benzyl-p-toluidine hydrochloride with ammonium thiocyanate and water, crystallises in colourless needles, m. p. 155·5°, and is converted by the action of ω-bromoacetophenone in warm alcoholic solution into 2-p-*tolylbenzylamino-4-phenylthiazole*,

$$\begin{array}{c} CPh·N \\ \| \quad \quad \rangle C·N(C_6H_4Me)·CH_2Ph, \\ CH—S \end{array}$$
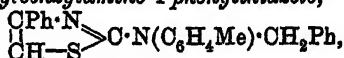
which forms large prisms, m. p. 125°, and yields a *hydrochloride*, a *picrate*, m. p. 155°, and a *platinichloride*, m. p. 225° (decomp.).

2-p-*Tolylimino-4-phenyl-3-benzylthiazoline*,

$$\begin{array}{c} C_6H_4Me·N:C——N·CH_2Ph \\ S·CH:CPh \end{array}$$
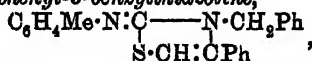
prepared from *s*-p-tolylbenzylthiocarbamide and ω-bromoacetophenone, forms colourless needles, m. p. 152°; the *hydrochloride*, *platinichloride*, m. p. 233° (decomp.), and *picrate*, m. p. 155°, are described. That the compound has the above constitution, and not that of the isomeric 2-benzylimino-4-phenyl-3-p-tolylthiazoline, has been established by its behaviour towards carbon disulphide, which at 200° leads to the removal of the p-tolylimino-group as p-tolylthiocarbimide and the formation of 2-*thion-4-phenyl-3-benzylthiazoline*, $\begin{array}{c} S——CS \\ \quad \quad \rangle N·CH_2Ph, \\ CH:CPh \end{array}$ which crystallises in pale yellow needles, m. p. 101°.

When heated with benzyl chloride for eight hours at 175°, 2-p-toluidino-4-phenylthiazole yields 2-p-*tolylbenzylamino-4-phenyl-5-benzylthiazole*, $\begin{array}{c} CPh——N \\ \| \quad \quad \rangle C·N(C_6H_4Me)·CH_2Ph. \\ C(CH_2Ph)·S \end{array}$ This forms needles, m. p. 125°, and is accompanied by 2-p-*toluidino-4-phenyl-5-benzylthiazole*, $\begin{array}{c} CPh——N \\ \| \quad \quad \rangle C·NH·C_6H_4Me, \\ C(CH_2Ph)·S \end{array}$ which crystallises in needles, m. p. 174°, and yields a *platinichloride*, m. p. 203° (decomp.), and a *picrate*, m. p. 151°.

That the introduction of the benzyl group has taken place in the thiazole ring and not in the *p*-toluidino-residue has been proved in the case of the last-mentioned thiazole by the formation of an *acetyl* derivative, $C_{25}H_{22}ON_2S$, m. p. 144°, and also by the removal of the *p*-tolylimino-group as *p*-tolylthiocarbimide when the thiazole is heated with carbon disulphide.

2-p-*Tolylimino-4-phenyl-3-methylthiazoline*,

$$\begin{array}{c}CPh\cdot NMe\\ \| \qquad\qquad\ \diagdown\!\!\!\!> C\!:\!N\cdot C_6H_4Me,\\ CH\!\!-\!\!\!-\!\!\!-\!\!S\end{array}$$
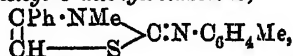
obtained in the form of its *methiodide*, large needles, m. p. about 200° (decomp.), by heating 2-*p*-toluidino-4-phenylthiazole with methyl iodide in methyl alcoholic solution, crystallises in colourless leaflets, m. p. 118°. It has also been prepared by the condensation of *s-p*-tolylmethylthiocarbamide with ω-bromoacetophenone; the *hydrochloride* and *picrate*, m. p. 158°, are described. When heated with carbon disulphide, it yields *p*-tolylthiocarbimide and 2-*thion-4-phenyl-3-methyl-thiazoline*,

$$\begin{array}{c}CS\cdot NMe\\ \| \qquad\qquad\ \diagdown\!\!\!\!> CPh,\\ S\!\!-\!\!\!-\!\!CH\end{array}$$

which crystallises in pale yellow needles, m. p. 127°.

2-p-*Tolylimino-4-phenyl-5-benzyl-3-methylthiazoline*,

$$\begin{array}{c}CPh\!\!-\!\!\!-\!\!\!-\!\!NMe\\ \| \qquad\qquad\qquad\ \diagdown\!\!\!\!> C\!:\!N\cdot C_6H_4Me,\\ C(CH_2Ph)\cdot S\end{array}$$
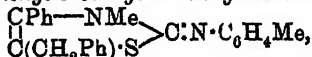
prepared by the action of methyl iodide on 2-*p*-tolylimino-4-phenyl-5-benzylthiazole, forms colourless prisms, m. p. 151°, and yields a *hydrochloride*, and a *methiodide*, crystallising in needles, m. p. about 250° (decomp.). It is resolved by carbon disulphide into *p*-tolylthiocarbimide, and 2-*thion-4-phenyl-5-benzyl-3-methylthiazoline*,

$$\begin{array}{c}NMe\cdot CPh\\ \| \qquad\qquad\ \diagdown\!\!\!\!> C\cdot CH_2Ph,\\ CS\!\!-\!\!\!-\!\!\!-\!\!S\end{array}$$

which forms silvery, lustrous leaflets, m. p. 116°.

5-*Bromo-* 2 - p - *toluidino-4-phenylthiazole*, obtained by brominating 2 -*p*- toluidino - 4 - phenylthiazole in benzene solution, crystallises in colourless leaflets or needles, which melt and decompose at 134°, yielding *p*-tolylthiocarbimide; the *hydrobromide*, m. p. 179° (decomp.), and *acetyl* derivative, m. p. 142·5°, crystallise in colourless prisms. It is reduced by zinc and acetic acid to the original thiazole. Attempts to prepare the bromothiazole by the condensation of *p*-tolylthiocarbamide with di-ω-bromoacetophenone yielded a *substance*, m. p. 142° (decomp.).

When warmed with amyl nitrite in alcoholic solution, 2-*p*-toluidino-4-phenylthiazole yields the 5-*nitroso*-derivative,

$$\begin{array}{c}CPh\!\!-\!\!\!-\!\!N\\ \| \qquad\quad\ \diagdown\!\!\!\!> S\cdot NH\cdot C_6H_4Me.\\ C(NO)\cdot S\end{array}$$
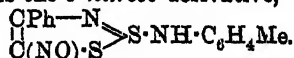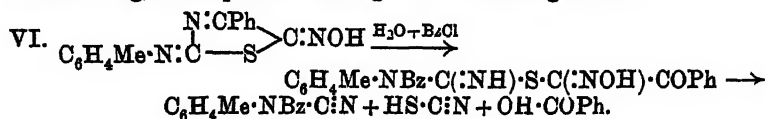
This separates in yellowish-brown leaflets, m. p. 184° (decomp.), yields a *hydrochloride*, red needles, an *acetyl* derivative, lustrous, dark red leaflets, m. p. 163°, and is reduced by zinc and acetic acid in alcoholic solution to the corresponding *amino*-compound, which, however, could not be isolated in a pure condition.

On treatment with cold aqueous alkalis it becomes brown, probably owing to the formation of salts derived from the tautomeric form (see VI, next page); when boiled with aqueous alkalis it undergoes com-
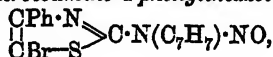
plete decomposition, yielding hydrogen sulphide, p-tolylthiocarbimide, carbon dioxide, thiocyanic acid, benzoic acid, ammonia, and p-toluidine.

The *silver* salt, $C_{16}H_{12}ON_3SAg$, prepared by treating an alcoholic solution of the nitroso-compound with the equivalent amounts of ammonia and silver nitrate, separates as an indistinctly crystalline, red precipitate which readily decomposes and explodes when rapidly heated.

On treatment with benzoyl chloride, a solution of the nitroso-compound in aqueous alkalis yields benzoyl-p-tolylcyanamide (Heller and Bauer, A., 1902, i, 444), benzoic and thiocyanic acids. This reaction, which establishes the position of the nitroso-group in the thiazole ring, takes place according to the following scheme :

VI. $C_6H_4Me \cdot N : C \underset{S}{\overset{N : CPh}{\diagdown}} C : NOH \xrightarrow{H_2O + B_4Cl}$

$C_6H_4Me \cdot NBz \cdot C(: NH) \cdot S \cdot C(: NOH) \cdot COPh \longrightarrow$
$C_6H_4Me \cdot NBz \cdot C : N + HS \cdot C : N + OH \cdot COPh.$

5-Bromo-2-p-tolylnitrosoamino-4-phenylthiazole,
$\underset{CBr-S}{\overset{CPh \cdot N}{\diagdown}} C \cdot N(C_7H_7) \cdot NO,$

prepared by warming 5-bromo-2-p-toluidino-4-phenylthiazole with amyl nitrite, forms colourless needles, m. p. 220°.

2-p-Toluidino-4-phenylthiazole combines with benzenediazonium chloride in alcoholic solution, yielding *5-benzeneazo-2-p-toluidino-4-phenylthiazole,* $C_6H_4Me \cdot NH \cdot C \underset{S}{\overset{N \cdot CPh}{\diagdown}} C \cdot N : NPh$, which crystallises in orange-red needles, m. p. 191°, and forms an *acetyl* derivative, $C_{24}H_{20}ON_4S$, red prisms, m. p. 217°, and a *hydrochloride*, crystallising in dark violet-red needles having a greenish glance, m. p. 184° (decomp.).

5-p-Nitrobenzeneazo-2-p-toluidino-4-phenylthiazole, obtained in a similar manner from p-nitrobenzenediazonium chloride, crystallises in dark red needles, m. p. 245° (decomp.) ; the *hydrochloride*, reddish-violet needles, and *acetyl* derivatives, red needles, both melt indefinitely at 250°.

The authors have also studied the behaviour of the remaining aminothiazoles and iminothiazolines described in this paper towards diazonium salts, and find that the iminothiazolines in no circumstances couple with the diazonium salts, whilst the aminothiazoles, in which the 5-position is unsubstituted, readily combine, yielding azo-compounds. The behaviour of 5-bromo-2-p-toluidino-4-phenylthiazole is, however, exceptional, the action of benzenediazonium chloride leading to the removal of the bromine atom and the formation of the above-mentioned 5-benzeneazo-2-p-toluidino-4-phenylthiazole. The reaction towards diazonium salts thus furnishes a ready means of distinguishing whether the product obtained by the condensation of a monosubstituted thiocarbamide with ω-bromoacetophenone and analogous halogeno-ketones is an aminothiazole or iminothiazoline.
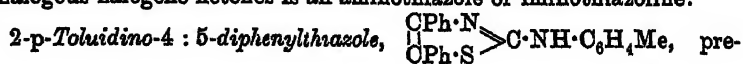
2-p-*Toluidino*-4 : 5-*diphenylthiazole,* $\underset{CPh \cdot S}{\overset{CPh \cdot N}{\diagdown}} C \cdot NH \cdot C_6H_4Me$, pre-

pared from desyl bromide and *p*-tolylthiocarbamide, crystallises in colourless needles, m. p. 178°, and forms a *hydrochloride*.

The condensation of ω-bromoacetophenone and allylthiocarbamide yields 2-*allylamino*-4-*phenylthiazole*, $\begin{matrix} CPh \cdot N \\ \| \quad \quad \searrow C \cdot NH \cdot C_3H_5 \\ CH \!\!-\!\! S \end{matrix}$, which has m. p. 73°, and couples with diazonium salts to form red azo-compounds.　　　　　　　　　　　　　　　　　　　　　　　　　F. B.

Decomposition of Alkylidenehydrazines. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1754—1759).—*Menthylidene-hydrazine*, $CH_2 \!\!<\!\! \begin{matrix} CH_2 \cdot CHPr \\ CHMe \cdot CH_2 \end{matrix} \!\!>\!\! C{:}N \cdot NH_2$, is a colourless liquid, b. p. 144°/30 mm., 248—249°/759 mm., D_0^{20} 0·9333, n_D 1·4940, $[\alpha]_D - 52\ 45°$. When distilled under reduced pressure, it leaves a viscous residue which, on treatment with 10% sulphuric acid in the cold, yields menthone and *l*-menthazine (compare A., 1908, i, 91). Pure menthylidenehydrazine yields no menthazine with cold 10% sulphuric acid, the sole product being menthone, which exhibits a low specific rotation owing to partial inversion. Distillation of the base with platinised porous tile yields hydrazine and *l*-menthazine. Menthylidenehydrazine is slightly decomposed, with evolution of nitrogen, when distilled with fused potassium hydroxide, whilst in presence of both platinised porous tile and fused alkali, it is resolved into nitrogen and menthane.

*iso*Thujylidenehydrazine, $CMe \!\!<\!\! \begin{matrix} CHPr^{\beta} \cdot CH_2 \\ CMe \!\!-\!\! C{:}N \cdot NH_2 \end{matrix}$, prepared from *iso*thujane and hydrazine hydrate, is a faint yellow, viscous liquid, b. p. 143—144°/17 mm., 152—153°/25 mm., D_0^{20} 0·9579, n_D 1·5328. Distillation of the base in presence of potassium hydroxide, spongy platinum, or molecular silver yields (1) nitrogen, (2) hydrazine, (3) a mixture of the hydrocarbons, $C_{10}H_{18}$ and $C_{10}H_{16}$, giving a cherry-red coloration with sulphuric acid and acetic anhydride and a green one with sulphuric acid and methyl alcohol, and (4) iso*thujazine*,

$$C_{10}H_{16}{:}N_2{:}C_{10}H_{16},$$

which crystallises in golden-yellow needles, m. p. 161—162°.

When distilled with potassium hydroxide, carvylidenehydrazine yields a *hydrocarbon*, $C_{10}H_{16}$, b. p. 175—176°/749 mm. (175—176°/757 mm.), D^{20} 0·8361 (0·8349), n_D 1·4678 (1·4665), $[\alpha]_D - 36·74°$ (−35·36°), which with hydrogen bromide gives the *dipentene hydrobromide*, $C_{10}H_{16},2HBr$, m. p. 63°, and with ethyl nitrite and hydrochloric acid, *l*-limonene β-nitrosochloride.　　　　　　　\ T. H. P.

Hydantoins. XX. Action of Thiocyanates on α-Amino-acids. TREAT B. JOHNSON (*Amer. Chem. J.*, 1913, **49**, 68—69).—It has been shown in earlier papers that by the action of thiocyanates on acyl derivatives of α-amino-acids, acylthiohydantoins are produced. The author has now found that the salt used in certain experiments (A., 1912, i, 53, 316, 390, 807) which was supposed to be potassium thiocyanate was really the ammonium salt, and the yields recorded were therefore obtained from the latter. The two salts show a remarkable difference in their behaviour with hippuric acid; the same com-

pound is formed in each case, but with the potassium salt it is obtained as an oily product which only slowly solidifies, whilst when prepared from the ammonium salt it solidifies at once on being poured into water.   E. G.

Tetraphenyldi-iminotetrahydromiazthiole (3:5-Diphenyl-imino-1:4-diphenyltetrahydro-1:2:4-thiodiazole). EMIL FROMM [with WILHELM BITTERICH] (*Annalen*, 1912, **394**, 284—290).— 3:5-Diphenylimino-1:4-diphenyltetrahydro-1:2:4-thiodiazole is probably a direct product of the oxidation of diphenylthiocarbamide, and is not formed through the intermediate production of an unstable disulphide (compare Fromm and Heyder, A., 1909, i, 903). It is best prepared by Hugershoff's method of oxidation by alcoholic bromine, care being taken to work in the cold, otherwise triphenylguanidine is obtained. The substance is converted into triphenylguanidine by concentrated hydrochloric acid, and is decomposed by boiling glacial acetic acid into acetanilide and 1-anilinobenzothiazole. By heating with aniline at 110° for several hours, the diphenyliminodiphenyltetrahydrothiodiazole is converted into the isomeric *triphenylguanidobenzothiazole*, NHPh·C(:NPh)·NPh·C$\underset{S}{\overset{N}{<}}C_6H_4$, m. p. 142°, which is not desulphurised by lead oxide and an alkali, and yields by the Schotten-Baumann process 2-*benzoylphenylaminobenzothiazole*,

$$C_6H_4\underset{S}{\overset{N}{<}}C·NPh·COPh,$$
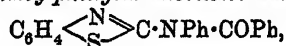
m. p. 156°, which is also obtained from 2-anilinobenzothiazole, benzoyl chloride, and aqueous sodium hydroxide.   C. S.

Trimethylparamide. HANS MEYER and KARL STEINER (*Ber.*, 1912, **45**, 3676—3677. Compare Mumm and Bergell, A., 1912, i, 1015).—Trimethylparamide can be prepared in a pure condition by heating methylamine mellitate for two hours in a sealed tube at 200° and recrystallising the colourless product from chlorobenzene; it is quantitatively hydrolysed to mellitic acid on prolonged boiling with potassium hydroxide solution.   D. F. T.

Disulphides with Neighbouring Double Linkings. Derivatives of Dithiobiurets and of Thiurets. EMIL FROMM [and RICHARD HEYDER, ADOLF JUNG, and MARGRET STURM] (*Annalen*, 1912, **394**, 258—284).—Since only one example is known of the simultaneous production of an arylguanidoarylthiocarbamide and a diarylguanidothiocarbamide by the decomposition of an arylthiuret by an aromatic amine (A., 1908, i, 700), the action of different aromatic amines on a series of thiurets has been examined. It is found that, as a rule, the two products of the decomposition are formed when the arylthiuret and the aromatic amine contain the same aromatic group.

o-*Anisyldithiobiuret*, C$_9$H$_{11}$ON$_5$S$_2$, m. p. 153°, yellowish-white needles, obtained by heating equal weights of perthiocyanic acid and o-anisidine on the water-bath, is converted by boiling hydrochloric acid and ferric chloride into o-*anisylthiuret hydrochloride*, C$_9$H$_9$ON$_5$S$_2$,HCl, m. p. 220° (hydrated) or 235° (anhydrous). The latter and o-anisidine in

boiling alcohol yield sulphur, o-*anisylguanido-o-anisylthiocarbamide,*
OMe·C_6H_4·NH·CS·NH·C(:NH)·NH·C_6H_4·OMe (the constitution of
which is proved by its conversion into o-*anisylguanido-o-anisyl-ψ-
benzylthiocarbamide,*
OMe·C_6H_4·N:C(S·C_7H_7)·NH·C(:NH)·NH·C_6H_4·OMe,
m. p. 116°, by boiling with benzyl chloride and an excess of aqueous
alcoholic sodium hydroxide), and *di-o-anisylguanidothiocarbamide,*
which is isolated as the *hydrochloride,*
C(NH·C_6H_4·OMe)$_2$:N·CS·NH$_2$,HCl,
m. p. 205°. By boiling this hydrochloride with lead oxide and
alcoholic sodium hydroxide, *di-o-anisyldicyanodiamide,*
CN·N:C(NH·C_6H_4·OMe)$_2$,
m. p. 168°, white needles, is obtained. In a similar manner, *p*-phene-
tylthiuret hydrochloride and *p*-phenetidine in boiling alcohol yield
di-p-phenetylguanidothiocarbamide, m. p 142° (*hydrochloride,* m. p. 167°),
and p-*phenetylguanido-p-phenetylthiocarbamide,* m. p. 172°, of which the
former is converted into *di-p-phenetyldicyanodiamide,* m. p. 176°, by
lead oxide and alcoholic sodium hydroxide, and the latter into p-*phenetyl-
guanido-p-phenetyl-ψ-benzylthiocarbamide,* m. p. 180°, by benzyl chloride
and alcoholic sodium hydroxide. *p*-Phenetylthiuret hydrochloride and
aniline react to form phenylguanido-*p*-phenetylthiocarbamide, m. p.
184°, not 170° (A., 1907, i, 982), and a small amount of *phenyl-p-
phenetylguanidothiocarbamide,* OEt·C_6H_4·NH·C(NHPh):N·CS·NH$_2$,
m. p. 137°, the *hydrochloride* of which, $C_{16}H_{18}ON_4S$,HCl,H$_2$O, has m. p.
113—114°.

p-Phenetylguanidophenylthiocarbamide (*loc. cit.*) has m. p. 158°,
not 168°, and forms a *hydrochloride,* m p. 168°.

o-*Tolylthiuret hydrochloride,* $C_9H_9N_3S_2$,HCl,2H$_2$O, m. p. 175°, obtained
from *o*-tolyldithiobiuret and boiling hydrochloric acid and ferric
chloride, reacts with *o* toluidine in boiling alcohol to form *tri-o-tolyl-
diguanide hydrochloride,* $C_{23}H_{25}N_5$HCl, m. p. 233°, from which *tri-o-
tolyldiguanide,* C(NH·C_6H_4Me)$_2$·N·C(:NH)·NH·C_6H_4Me, m. p. 179°,
is liberated by ammonia. The by-product of the preceding reaction is
di-o-tolylguanidothiocarbamide, m. p. 172°, or o-*tolylguanido-o-tolylthio-
carbamide,* $C_{16}H_{18}N_4S$,EtOH, m. p. 178°, according to the dilution of
the solution. *o*-Tolylthiuret and aniline in boiling alcohol yield only
phenylguanido-o-tolylthiocarbamide, m. p. 135° (*hydrochloride,* m. p. 183°),
and phenylthiuret and *o*-toluidine under similar conditions yield only
phenyl-o-tolylguanidothiocarbamide, m. p. 111° (*hydrochloride,* m. p.
89°). *Phenylguanido-o-tolyl-ψ-benzylthiocarbamide,* $C_{22}H_{22}N_4S$, m. p.
124°, crystallises in yellow octahedra.

The following substances have been obtained by the interaction of
arylthiuret hydrochlorides and phenylhydrazine in boiling alcohol
(A., 1907, i, 982; 1908, i, 700), and are converted into triazole
derivatives by boiling aqueous alcoholic alkalis; thus *o*-tolylthiuret
hydrochloride and phenylhydrazine yield *anilguanido-o-tolylthiocarb-
amide* or *anil-o-tolylguanidothiocarbamide,*
NHPh·NH·C(:NH)·NH·CS·NH·C_6H_4Me or
NHPh·NH·C(NH·C_6H_4Me):N·CS·NH$_2$, m. p. 157° [3 : 5(or 5 : 3-)-
amino-o-toluidino-]-*phenyltriazole,* NPh$\genfrac{}{}{0pt}{}{N{=\!=\!=\!=}C·NH_2}{C(NH·C_6H_4Me):N}$ or

NPh$\underset{C(NH_2):N}{\overset{N=\!\!=\!\!=C:NH·C_6H_4Me}{\diagdown}}$, has m. p. 143°] ; o-anisylthiuret and

phenylhydrazine yield two substances which could not be obtained pure, but have been converted into 5-*amino*-3-*o-anisidino* 1-*phenyltriazole*,

OMe·C$_6$H$_4$·NH·C$\underset{N:C·NH_2}{\overset{N·NPh}{\diagdown}}$, and 3-*amino*-5-*o-anisidino*-1-*phenyl-triazole*, one of which forms a sparingly soluble *hydrochloride*,

$$C_{15}H_{15}ON_5,HCl,H_2O,$$

m. p. 228°, and a *picrate*, m. p. 250°, red needles, and the other an easily soluble *hydrochloride*, and a *picrate*, m p. 169° ; *p*-phenetyl-thiuret hydrochloride and phenylhydrazine (Fromm and Vetter, A., 1907, i, 982) yield anilguanido-*p*-phenetylthiocarbamide or anil-*p*-phenetylguanidothiocarbamide, m. p. 170°, not 168°, and aminophenyl-guanido-*p*-phenetylthiocarbamide or aminophenyl-*p*-phenetylguanido-thiocarbamide, m. p. 168°, white needles (not m. p. 236°, white leaflets), the latter forming a *benzylidene* derivative, m. p. 183°.

The formation of 3-amino-5-thiol-1-phenyltriazole, m. p. 234°, and dianildithiobiuret, m. p. 178°, from phenylhydrazine and phenyl-methylthiuret has already been recorded (A., 1908, i, 700). The former reacts with benzyl chloride and aqueous sodium hydroxide to form 3-*amino*-5-*benzylthiol* 1-*phenyltriazole*, m. p. 116°, and with benzoyl chloride and aqueous sodium hydroxide to form 3-*benzoylamino*-5-*thiol*-1-*phenyltriazole*, m. p. 267°, from which 3-*benzoylamino*-5-*benzyl-thiol*-1-*phenyltriazole*, m. p. 161°, is obtained by means of benzyl chloride and aqueous sodium hydroxide. The action of benzoyl chloride and sodium carbonate on dianildithiobiuret or on 3-thiol-5-phenylhydrazino-1-phenyltriazole yields 3-*thiol*-5-*benzoylphenylhydr-azino*-1-*phenyltriazole*, NHPh·NBz·C$\underset{N\!-\!\!-\!C·SH}{\overset{NPh·N}{\diagdown}}$, m. p. 218°, which

yields the 3-*benzylthiol* derivative, m. p. 171°, by boiling with benzyl chloride and the calculated quantity of aqueous alcoholic sodium hydroxide, and 3-*benzylthiol*-5-*phenylhydrazino* 1-*phenyltriazole*, m. p. 118°, red needles, when an excess of the alkali is employed. The substance, m. p. 218°, obtained by the action of acetic anhydride on dianildithiobiuret (*loc. cit.*) is 3-*thiol*-5-*acetylphenylhydrazino*-1-*phenyl-triazole* ; by treatment with benzyl chloride and an alkali, it yields 3-*benzylthiol*-5-*acetylphenylhydrazino*-1-*phenyltriazole*, m. p. 102°, yellow leaflets. The constitution of the oxidation product, m. p. 218°, of 3-thiol-5-phenylhydrazino-1-phenyltriazole as a benzeneazotriazole (*loc. cit.*) is proved as follows. In the presence of an alkali, the sub-stance is converted into 5-*benzeneazo*-3-*thion*-2-*benzoyl*-1-*phenyltriazole*,

PhN$_2$·C$\underset{N\!-\!\!-\!CS}{\overset{NPh·NBz}{\diagdown}}$, m. p. 167°, red needles, by benzoyl chloride, and

into 5 *benzeneazo*-3-*benzylthiol*-1-*phenyltriazole*,

$$PhN_2·C\underset{N\!-\!\!-\!C·SC_7H_7}{\overset{NPh·N}{\diagdown}},$$
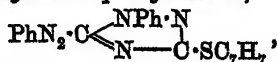
m. p. 116°, reddish-yellow leaflets, by benzyl chloride. The latter is also produced when the former is treated with benzyl chloride and an alkali. The oxidation product can be acylated or alkylated, but not

both simultaneously, thus proving that the same hydrogen atom is concerned in each process and that the substance is tautomeric.

The base $C_{14}H_{13}N_5S$, m. p. 181°, which is obtained together with the preceding azo-compound by the action of boiling hydrochloric acid on dianildithiobiuret (*loc. cit.*), forms, in addition to the diacetyl and the dibenzylidene derivatives already described, a *dibenzoyl* derivative, m. p. 216°, does not react with benzyl chloride in the presence of an alkali, and requires 2 mols. of sodium nitrite for its diazotisation. These facts are contrary to the formula previously ascribed to the base, and are more in harmony with the constitution :

$$NH_2 \cdot C_6H_4 \cdot N\text{:}C\underset{NH}{\overset{-S}{<}}C\text{:}N \cdot C_6H_4 \cdot NH_2.$$
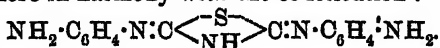
Under the influence of hydrogen chloride, substituted dithiobiurets react with aldehydes or ketones to form aldurets or keturets (A, 1893, i, 575; 1906, i, 656), which can be alkylated in consequence of the presence of the thiol groups; thus *o*-tolyldithiobiuret and acetone yield *o-tolyldimethyl-ψ-dithioketuret*, $C_6H_4Me \cdot N\text{:}C(SH) \cdot N\underset{CMe_2}{\overset{C(SH)}{<}}N$, m. p. 236°, which forms a *benzyl* derivative. m. p. 192°, and a *dibenzyl* derivative, m. p. 83°; *o*-tolyldithiobiuret and benzaldehyde yield *phenyl-o-tolyl-ψ-dithioalduret*, $C_6H_4Me \cdot N\text{:}C(SH) \cdot N\underset{CHPh}{\overset{C(SH)}{<}}N$, m. p. 207°, yellow leaflets (*dibenzyl* derivative, m. p. 118°); *o*-tolyldithiobiuret and 40% formaldehyde yield *o-tolyl-ψ-dithioalduret*,

$$C_6H_4Me \cdot N\text{:}C(SH) \cdot N\underset{CH_2}{\overset{C(SH)}{<}}N,$$
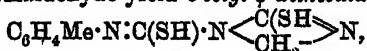
m p. 197°, yellow leaflets (*dibenzyl* derivative, m. p. 80°). o-Tolyl-dithiobiuret does not react with acetophenone or benzophenone.

C. S.

Crystallographic Study of the Sodium Salt of *iso*Hydroxy-tetrazole. ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 645—648).—The author has studied the salt $CHON_4Na,3H_2O$, which was obtained by Palazzo (A., 1910, i, 342). The salt loses its water at 120—130°, and explodes at 240°. It occurs in two crystalline forms: (1) pale straw-yellow tablets belonging to the pinacoidal class of the triclinic system; $a:b:c = 1\cdot2494:1:0\cdot8521$, α 130°6′, β 114°47′, γ 79°34·5′; (2) colourless tablets, also belonging to the pinacoidal class of the triclinic system ;

$a:b:c = 0\cdot6798:1:1\cdot0834$, α 54°53′, β 124°32·5′, γ 121°43′.

R. V. S.

Action of Chlorine on Ethyl Phenylazoacetoacetate. A New Way to Prepare Derivatives of Formimido-chloride. CARL BÜLOW and PETER NEBER (*Ber.*, 1912, 45, 3732—3744).— Elimination of the carbethoxyl group takes place when ethyl phenyl-azoacetoacetate is hydrolysed by sodium hydroxide (Richter and Münzer, A., 1884, 1342) or brominated (Hecking, *Diss.*, 1910). The action of chlorine, however, results in the removal of the acetyl group and the formation of the dichlorophenylhydrazone of ethyl mono-chloroglyoxylate. When this substance is completely reduced,

2 : 4-dichloroaniline is formed, and the compound may also be synthesised from this base. The remaining chlorine atom must necessarily be attached to the α-carbon atom of the side-chain, and it is very reactive. It may be replaced by an amino-group, more prolonged action of ammonia replacing, in addition, the ester group.

A method is given for the preparation of ethyl phenylazoaceto-acetate. Chlorination may be effected in glacial acetic acid by chlorine or sulphuryl chloride, but the best results are obtained by chlorine in chloroform. The 2 : 4-*dichlorophenylhydrazone* of *ethyl α-chloroglyoxylate*, $C_6H_3Cl_2·NH·N:CCl·CO_2Et$, crystallises in brilliant needles, m. p. 98°. When treated with alcoholic potash, hydrogen chloride is eliminated, and a *product*, $C_{10}H_8O_2N_2Cl_2$, is obtained in beautiful yellow needles, m. p. 196°. Its constitution is probably represented by the annexed formula. The 2 : 4-*dichlorophenylhydrazone* of *ethyl α-amino-glyoxylate*, $C_{10}H_{11}O_2N_3Cl_2$, which is immediately formed when alcoholic ammonia is added to the imido-chloride, crystallises in long, flat needles from dilute ethyl acetate, m. p. 99°, and is readily soluble in mineral acids, but does not form a diazonium salt. More prolonged action of ammonia results in the formation of the *amide*, $C_6H_3Cl_2·NH·N:C(NH_2)·CO·NH_2$, in long, grey needles, m. p. 170°.
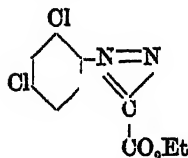
Ethyl 2 : 4-*dichlorobenzeneazoacetoacetate*, $C_6H_3Cl_2·N_2·CHAc·CO_2Et$, may be prepared in a similar manner by condensing the diazotised dichloroaniline with ethyl acetoacetate. It crystallises in yellow needles, m. p. 127°, and gives the above α-chloro-compound with chlorine. When condensed with hydrazine hydrate, it gives 4-o-p-*dichlorobenzeneazo-5-hydroxy-3-methylpyrazole*, $C_{10}H_8O_2N_3Cl_2$, in orange-yellow needles, m. p. 207°, which cannot be precipitated by water from piperidine, in which the substance is very soluble.

Similarly, phenylhydrazine yields 4-o-p-*dichlorobenzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole*, $C_{16}H_{12}ON_4Cl_2$, in brick-red needles, m. p. 195°, which concentrated nitric acid converts into 2 : 4-dichlorophenyl-diazonium chloride and 4-nitro-1-benzene-3-methylpyrazolone (compare A., 1910, i, 902). J. C. W.

The Racemisation of Proteins and their Derivatives Resulting from Tautomeric Change. I. HENRY D. DAKIN (*J. Biol. Chem.*, 1912, 13, 357—362).—There is an analogy between the hydantoin, $NH<^{CO-NH}_{CRH·CO}$, and peptide,

$$RCH<^{NH·CO-}_{CO·NH·CHR·CO_2H},$$
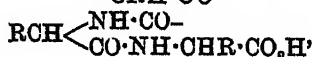
groupings, in both of which the –CH·CO– group can exhibit keto-enolic tautomerism and hence racemisation (compare Dakin, A., 1910, i, 590). In the peptide complex the terminal amino-acid containing a free carboxyl group cannot, however, undergo this change. Such tautomeric change apparently takes place when a protein is digested at low temperatures with dilute alkali (compare Kossel and Weiss, A., 1909, i, 542; 1910, i, 791).

The optical rotatory power of gelatin falls to a minimum when it is digested with dilute alkali. On subsequent hydrolysis with acids, inactive leucine, aspartic acid, arginine, histidine, and phenylalanine are obtained, whereas proline, glutamic acid, and lysine are obtained in the optically active forms together with part of the alanine. The conclusion is drawn that none of the carboxyl groups in the substances which were obtained inactive are free in gelatin. On the other hand, glutamic acid, lysine, and alanine may have some of their carboxyl groups free, that is, they may occupy terminal positions in the peptide chains. An alternative is that these amino acids are rapidly liberated in the free state by the hydrolytic action of the alkali and so escape racemisation. E. F. A.

The Refractive Indices of Solutions of Certain Proteins. VIII. Globin. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1913, 13 455—462).—Globin was prepared from ox-corpuscles by three different modifications of Schulz's method. The value of a for the purest preparation dissolved in decinormal potassium hydroxide or hydrochloric acid is 0.00169 ± 0.00005. W. D. H.

The Preparation and Properties of a Compound Protein; Globin Caseinate. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1913, 13, 499—506).—Globin caseinate may be prepared by mixing two parts of globin with one of casein, each in a faintly alkaline solution. It displays properties intermediate between those of the two component proteins, the acid function of globin being enhanced by union with casein and the basic function of casein by union with globin.

The compound is not decomposed by dilute acetic acid in the cold, but it is by boiling dilute acetic acid, or by pepsin and acetic acid. The change in the refractive index of decinormal potassium hydroxide due to the introduction of 1% of globin caseinate is 0.00162 ± 0.00005. The refractivity of a compound protein is an additive function of the refractivities of its components. W. D. H.

Constitution of the Blood and Bile Pigments. I. HANS FISCHER and ERICH BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1913, 83, 50—71).—The formation of tri- and tetra-substituted pyrroles on the decomposition of hæmin is explained on the hypothesis that the pyrrole nuclei are united by a CH_2 radicle in the 2-positions. Such 2- and 3-methylene derivatives have been synthesised by Colacicchi (A., 1912, i, 491).

Bis-(5-acetyl-2 : 4-dimethylpyrryl)methane, in which the methylene group is in the 3-position, resists the reducing action of hydrogen iodide and acetic acid during two hours. To some extent the a-acetyl residue is eliminated and *bis-(2 : 4-dimethylpyrryl-3 : 3')methane*,

$$NH\begin{matrix} OMe:C—CH_2—C:CMe \\ CH=CMe \quad MeC=CH \end{matrix}NH,$$

is formed. This compound has many of the properties of hemibilirubin; it gives the aldehyde reaction, is unstable, shows the urobilin bands, and the fluorescence reaction with zinc acetate. It forms a *picrate* and an a-azo-dye.

When the action of the reducing agent is prolonged for fourteen to sixteen hours, 2 : 3 : 4-trimethylpyrrole admixed with some 2 : 4-dimethylpyrrole is obtained.

Bis-(3-acetyl-2 : 4-dimethylpyrryl)methane (Colacicchi, *loc. cit.*) is readily reduced to pyrrole derivatives by acetic acid and hydrogen iodide. The mixture of pyrrole picrates was not separated.

Trialkylated pyrroles condense with formaldehyde in presence of alkali. The products are regarded as methylene derivatives, although the possibility of an alcohol structure, $NH\!\!<^{CMe\vdots C\cdot CH_2\cdot OH}_{CMe\vdots CMe}$, is not overlooked.

Tetramethylpyrrole was obtained on reducing the condensation product from 2 : 4 : 5-trimethylpyrrole; phyllopyrrole from the condensation product of cryptopyrrole.

2 : 3 : 5-*Trimethylpyrrole-4-propionic acid*,

$$NH\!\!<^{CMe\vdots C\cdot CH_2\cdot CH_2\cdot CO_2H}_{CMe\vdots CMe},$$
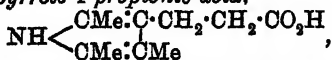
was not obtained on reducing the amorphous condensation product of formaldehyde with phonopyrrolecarboxylic acid, but it is readily formed on methylation of phonopyrrolecarboxylic acid. Tetramethylpyrrole is obtained at the same time.

The pyrrole, $CO_2Et\cdot C\!\!<^{CMe\vdots C—CH_2—C\,=CMe}_{CMe\cdot NH\quad\quad NH\cdot CMe}\!\!>C\cdot CO_2Et$, obtained by the action of formaldehyde on 3-carbethoxy-2 : 4-dimethylpyrrole, when boiled with acetic acid gives an intense green solution showing a characteristic band in the red similar to that of the copper salt of hemibilirubin.

Bis-5-acetyl-2 : 4-dimethylpyrrylethane,

$$NH\!\!<^{CMe=\!\!=\!\!C—CHMe—C=\!\!=\!\!CMe}_{C(COMe)\vdots CMe\quad\quad MeC\cdot C(COMe)}\!\!>NH,$$
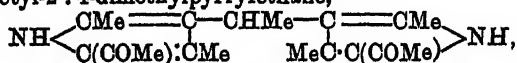
produced from 5-acetyl-2 : 4-dimethylpyrrole by the action of acetaldehyde, is decomposed by acetic acid and hydrogen iodide into 2 : 4-dimethylpyrrole. The formation of cryptopyrrole could not be determined.

All the foregoing pyrrole derivatives are decomposed by sodium methoxide, forming tetramethylpyrrole.

Tripyrrole is absolutely stable towards acetic acid and hydrogen iodide in the sense that no volatile bases are formed.

Bis-(2 : 4-dimethylpyrryl-3 : 3')methane crystallises in tiny pyramids and prisms, m. p. 139—140°; the *picrate* forms yellowish-brown needles, m. p. 125—126°.

2 : 3 : 5-*Trimethylpyrrole-4-propionic acid* forms a picrate, m. p. 126—127°.　　　　　　　　　　　　　　　　　　　　　　　　　E. F. A.

Bilirubin and Hæmin. WILLIAM KÜSTER [and P. DEIHLE] (*Zeitsch. physiol. Chem.*, 1912, 82, 463—483).—Sodium amalgam does not necessarily reduce vinyl groups, which remain unattacked during the conversion of hæmin into the leuco-compound or of bilirubin into hemibilirubin. The complex giving rise to methylethylmaleinimide on oxidation is contained already in bilirubin. One of the two complexes

in hæmin which gives hæmatic acid on oxidation loses carbon dioxide during conversion into bilirubin, and so gives rise to the imide when oxidised. On esterification with methyl alcohol and hydrochloric acid, bilirubin behaves differently from hæmin. A dimethyl derivative is obtained, in which one methyl replaces hydrogen, and the other is due to the addition of methyl alcohol.

The formulæ given by Piloty (A., 1912, i, 923) and by H. Fischer and Röse (A., 1912, i, 575) for bilirubic acid, etc., are discussed, and a complete structural formula for hæmin is suggested.

Pure mesoporphyrin yields methylethylmaleinimide on oxidation.

Bilirubin forms a silver salt containing 4 atoms of silver when fresh preparations are used ; older preparations react with 2 atoms only of silver. The salts have a metallic lustre, and the silver is not replaceable by barium. Bilirubin regenerated from the zinc salt dissolves in sodium hydrogen carbonate. This *aci*-form is more soluble in chloroform than the normal. *Dimethylbilirubin*, $C_{34}H_{40}O_7N_4$, is a blackish-green powder. E. F. A.

The Action of Yeast on Yeast-nucleic Acid. SAMUEL AMBERG and WALTER JONES (*J. Biol. Chem.*, 1913, 13, 441—446).— Yeast has no action on thymus-nucleic acid, but it causes the disappearance of yeast-nucleic acid. If compressed yeast is used, adenine and guanine appear ; if yeast powder is employed, adenine and guanosine are found. W. D. H.

Nucleases. III. PHŒBUS A. LEVENE and F. B. LA FORGE (*J. Biol. Chem.*, 1913, 13, 507—510).—The pyrimidine ribosides are more resistant towards the hydrolytic action of mineral acids than are the purine ribosides. Their behaviour to enzymes runs parallel to this. The differences towards acids can be removed by reducing the pyrimidine base in the riboside to the corresponding dihydropyrimidine. No tissue enzyme has, however, yet been discovered which hydrolyses either the original or the dihydro-derivative.

W. D. H.

Influence of the Reaction of the Medium on the Action of Ptyalin. WILHELM E. RINGER and H. VAN TRIGT (*Zeitsch. physiol. Chem.*, 1912, 82, 484—501).—The action of ptyalin on starch is studied in presence of varying amounts of sodium hydroxide and phosphoric acid, and the amount of reducing sugar formed contrasted with the hydrogen-ion concentration of the liquids as determined by the conductivity method. At 37° the optimum activity is observed in a solution having $p_H = 6.0$. When citrate is substituted for phosphate, the position of the optimum varies with the concentration of the citrate ; it is observed in more nearly neutral solutions with citrate than is the case with phosphate. In presence of sodium acetate and acetic acid the optimum is at $p_H = 6.0$. The presence of both phosphate and acetate reduces the amount of starch hydrolysis ; citrate has still more influence. The enzyme itself is not damaged during the duration of the experiment. When these are prolonged for five times as long, the position of the optimum is not materially altered. E. F. A.

Temperatures of Destruction of Emulsin in Ethyl Alcohol of Various Strengths. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], 7, 27—31).—A solution of emulsin in water was diluted with alcohol or alcohol and water to produce alcoholic liquids of various strengths containing the same quantity of emulsin. Portions of these liquids were then heated to various temperatures, and afterwards tested for activity on salicin. It was found that the temperature at which emulsin begins to become inactive under these conditions varies from 60° to 40° for liquids containing from 10 to 50% of alcohol, and remains constant at 45° to 40° for liquids containing 60 to 95% of alcohol. Total destruction of activity occurs at temperatures ranging from 70° to 55°. Different figures are obtained when the preparations are made by macerating emulsin in the alcoholic liquids   T. A. H.

Rennin. I. Properties of the Ferment when Prepared by Different Methods II. Acceleration of the Action of Rennin by Phosphoric Acid. III. The Variation in the Length of Time Required to Curdle Different Specimens of Milk A. ZIMMERMANN (*J. Ind. Eng. Chem.*, 1912, 4, 506—508).—The distinctive properties of rennin when prepared by the following different methods are described : (1) precipitated by sodium chloride, (2) precipitated by sodium sulphate, (3) rennin in scales (granular rennin), and (4) commercial rennin.

Phosphoric acid (0 075%) when added to milk increases the activity of the rennin, a property possessed in a less degree by lactic, hydrochloric, and oxalic acids.

The length of time required to curdle by the same specimen of rennin appears to be influenced by the length of time the milk has been kept; the staler the milk, the more rapid the action of the rennin ; this would appear to be a bacterial effect, yet it is found that a mixture of rennin and milk kept several hours at 40° will not curdle, whereas if the milk alone be subjected to this treatment, the addition of the same rennin causes rapid curdling.

The preparation of standardised rennin, the permanency of rennin solutions and of pepsin are also discussed.   F. M. G. M.

Antagonism between Citrates and Calcium Salts in Milk Curdling by Rennet. J. R KATZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 434—445).—Whilst $N/125$- and $N/25$-solutions of citric acid delay the curdling of milk more than two hours, the action is much weakened when substitution occurs at one of the active groups of the citric acid, and stops altogether when two or three of the groups are made inactive.

When substitution occurs at the alcohol group, the curdling is delayed three and a-half and nine and a-half hours respectively by $N/125$- and $N/25$-solutions. Similar results were obtained by tribasic acids not containing an alcohol group.

When substitution occurs at one carboxyl group in citric acid, a delay in curdling milk of one and a-quarter hours with $N/125$- and of six and a-half hours with $N/25$-solutions takes place. Results similar

to these were again obtained by employing dibasic acids with one or more alcohol groups.

The results show that when one active group is taken from citric acid, the characteristic action of the acid is reduced to about 6% of its original value, and that when two groups are substituted to about 1%.

<div align="right">N. H. J. M.</div>

Synthesising Action between Galactose and Ethyl Alcohol under the Influence of Kephir. EMILE BOURQUELOT and HENRI HÉRISSEY *Compt. rend.*, 1912, 155, 1552—1554).—β-Ethyl galactoside is slowly synthesised, in small quantities in the presence of kephir, from an alcoholic solution of galactose. The authors suggest that the synthesising agent in this case and also in that of emulsin obtained from almonds (compare A., 1912, i, 946) is really the lactase present in these two substances. <div align="right">W. G.</div>

Physiological Chemistry

Variations in the Irritability of the Reflex Arc. I. Variations under Asphyxial Conditions, with Blood-gas Estimations. E. L. PORTER (*Amer. J. Physiol.*, 1913, 31, 223—244).—The experiments were made on the spinal cat, subjected to asphyxial conditions. The records obtained offer no conclusive evidence of increased reflex irritability under asphyxia, but as the oxygen in the blood lessens and the carbon dioxide accumulates, the flexion reflex disappears. This is the general result, but the details differ according as the admixture of the two gases supplied varies. <div align="right">W. D. H.</div>

The Chemistry of Portal Blood. I. A Portal Fistula. EFIM S. LONDON and N. A. DOBROVOLSKAJA (*Zeitsch. physiol. Chem.*, 1912, 82, 415—416).—A description of the operative procedure in making a fistula for the obtaining of blood from the portal vein. Results will follow later. <div align="right">W. D. H.</div>

Glycolysis. III. PETER RONA and F. ARNHEIM (*Biochem. Zeitsch.* 1913, 48, 35—49. Compare A., 1911, ii, 619).—The authors confirm the previous statement that sugar is not destroyed by lysed corpuscles. They now show that if the corpuscles are previously lysed, they can still destroy sugar provided that phosphate or carbonate ions are present in sufficient concentration. They further show that the glycolysis is much diminished if intact corpuscles are diluted with physiological saline alone; if, however, carbonates or phosphates are added in sufficient concentration in a Ringer's fluid, when such a liquid is used to dilute the corpuscles, the glycolysis is not less than that produced by the undiluted corpuscles. The comparative glycolytic

properties of white and red corpuscles was also investigated. The red corpuscles diluted with saline to the volume of the original blood exerted nearly as great a glycolytic effect as the original blood, whereas the white corpuscles diluted to the same extent were almost inactive. Nevertheless, if the white corpuscles are diluted with a liquid containing phosphates, they exert a very marked glycolytic action. In the experiments carried out, no glycolytic power markedly superior to that of the red corpuscles could be demonstrated.

S. B. S.

The Alkalinity of Pancreatic and Intestinal Juice in Living Dogs. FRIEDRICH AUERBACH and HANS PICK (*Arb. K. Gesundheitsamte*, 1912, 43, 155—186).—Both these juices are strongly alkaline in spite of the blood being nearly neutral in reaction; the alkalinity was determined in the juices obtained from fistulæ in dogs by electrometric, colorimetric, and titrimetric methods. It corresponds with that of a sodium hydrogen carbonate solution, rather than with one of sodium carbonate. It is probable that the juices contain free carbon dioxide. The H-ion concentration averages $0\cdot5.10^{-8}$ mol./litre; the OH-ion concentration at 18° is about 10^{-6}, and at 37°, 5.10^{-6} mol./litre.

In intestinal juice, sodium chloride is more abundant than sodium hydrogen carbonate; in pancreatic juice the reverse obtains. The alkalinity of the duodenal contents corresponds with that which is the optimum for peptolytic (not tryptic) activity. W. D. H.

Effects of Nutrition with Maize. IV. Action of the Succus entericus of the Dog on Zein, Gliadin, Zeoses, and Gliadoses. SILVESTRO BAGLIONI [with G. AMANTEA and L. MANINI] (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 655—660. Compare A., 1911, ii, 999).—The *Succus entericus* of the dog has a weak digestive action on gliadin and an even weaker action on zein, but it has an almost equal digestive action on zeoses and gliadoses of peptic and tryptic origin. R. V. S.

Are the Endogenous Purine Substances the Products of the Activity of the Digestive Organs? FRANZ MAREŠ (*Pflüger's Archiv*, 1912, 149, 275—286).—Polemical against Sivén (A., 1912, ii, 780; compare following abstract). W. D. H.

The Source of Uric Acid in Man. II. FRANZ SMETÁNKA (*Pflüger's Archiv*, 1912, 149, 287—317).—This also is a reply to Sivén's criticism on the work of Mareš (A., 1910, ii, 973) and Smetánka (A., 1911, ii, 218). The article is mainly polemical, but does contain some fresh experimental work, and the main conclusions drawn are as follows. Intake of a purine-free diet causes an increase of purine excretion. This is due to nuclear catabolism occurring in and associated with the activity of the digestive glands. The increase lasts five to six hours after a meal; but when much protein is taken with the evening meal it may go on all night. The question whether variations in the protein intake produce variations in the purine

output is not definitely answered. Diets rich in starch act similarly, but less markedly. The original views of Mares on the question are considered to remain unshaken. W. D. H.

Animal Calorimetry. VII. The Metabolism of a Dwarf. FRANCIS H. McCRUDDEN and GRAHAM LUSK (*J. Biol. Chem.*, 1913, 13, 447—454).—A dwarf, suffering from infantilism, seventeen years old, and weighing 21 kilos., had a basal metabolism of 775 calories per square metre of body surface in twenty-four hours; this is about the same as in a dog. The metabolism was increased by 6·6% after food, and this again by 14·7% by reading illustrated periodicals in bed. The protein metabolism yielded the normal proportion of 15% of the total calories of heat-production. Nothing abnormal in metabolic processes was detected. W. D. H.

The Part Played by Acid in Carbohydrate Metabolism. Acid Diabetes. HERBERT ELIAS (*Biochem. Zeitsch.*, 1913, 45, 120—143).— Relatively small amounts of acids, administered to rabbits, can cause glycogen in large quantities to disappear from the liver; this disappearance results in hyperglycæmia and glycosuria in the animals The fact was established by the distinct positive results obtained in a series of researches in animals with livers rich in glycogen, whereas negative results were obtained from animals in which the livers were glycogen-free. The suprarenals take no part in this action, as positive results were obtained when dyspnœa was avoided, during chloral hydrate narcosis, and after cutting the splanchnics. In all cases, furthermore, the histological structure of the suprarenals remained intact. It was shown also, by perfusion experiments through the isolated liver, that adrenaline plays no part in the disappearance of the glycogen. The acid appears to act, therefore, directly on the liver itself. Perfusion experiments on the isolated liver of tortoises indicated that the glycogen separates from the liver cells for the most part unchanged when acid is added to the perfusion fluid.

S. B. S.

Has Heated Milk the Same Feeding Value as Raw Milk? EICHLOV (*Bied. Zentr.*, 1913, 42, 56—58; from *Mitt. deut. milchwirt. Ver.*, 1912).—Milk when heated loses the property of being coagulated by rennet, and the soluble calcium salts become insoluble; both changes presumably decrease the feeding value of milk.

Experiments in which dogs (ten days old) were fed for several months with fresh milk and boiled milk respectively gave the following results. The bones of the dogs fed with boiled milk, with one exception, contained less ash than when fed with fresh milk; the blood also contained less ash and only about half as much fibrin as the blood of the dogs which had fresh milk. When milk is heated for ninety minutes in boiling water, ammonia and hydrogen sulphide are produced in small amounts; the vapour from the heated milk also contained phosphorus. N. H. J. M.

The Influence of Standing or Lying on the Metabolism of Cattle. HENRY PRENTISS ARMSBY and J. AUGUST FRIES (*Amer. J. Physiol.*, 1913, 31, 245—253).—Details are given of the increase of metabolism in cattle when they are in a standing as compared with the lying position. The increased emission of heat during the standing periods is accompanied with a correspondingly increased elimination of both carbon dioxide and water.   W. D. H.

Nitrogen Retention on Feeding with Urea. EDUARD GRAFE and K. TURBAN (*Zeitsch. physiol. Chem.*, 1913, 83, 25—44).—A full account is given of metabolic experiments in dogs and pigs which show that retention of nitrogen occurs when urea is added to a carbohydrate rich diet. Sometimes equilibrium was attained; a small part of the nitrogen was excreted in the after period.   W. D. H.

Histochemistry of Spermatozoa. III. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1913, 83, 72—78).—Dried defatted spermatozoa from herrings consists as to three-quarters of nucleic acid and one-quarter of clupeine. The two compounds are united through the free amino-groups of the arginyl groups of the protamine.   E. F. A.

The Biochemistry of the Female Genitalia. I. The Lipins (Lipoids) of the Ovary and Corpus Luteum of the Pregnant and Non-pregnant Cow. JACOB ROSENBLOOM (*J. Biol. Chem.*, 1913, 13, 511—512).—Data are presented showing the percentages of fat, fatty acids, cholesterol, and lipoids in the ovary and corpus luteum of the cow. No increase in these occurs during pregnancy.   W. D. H.

The Sulphatide of the Brain. PHŒBUS A. LEVENE (*J. Biol. Chem.*, 1913, 13, 463—464).—The lipoid of the brain (ox), which contains sulphur, was isolated from the phosphatides; the method is not described. Elementary analyses are given which differ considerably from those of both Thudichum and W. Koch.   W. D. H.

The Influence of Quantity and Concentration of Poisons of the Digitalis Group on the Frog's Heart ARNOLD HOLSTE (*Arch. expt. Path. Pharm.*, 1912, 70, 435—438).—The experiments recorded show the importance of concentration as a factor.
          W. D. H.

Systole and Diastole of the Heart Under the Influence of Digitalin. ARNOLD HOLSTE (*Arch. expt. Path. Pharm.*, 1912, 70, 439—446).—It is stated that digitalin applied internally to the heart produces systolic standstill, and to the exterior, diastolic standstill. This has been explained by supposing that the outer layers of the cardiac muscle respond differently to the drug from the internal layers. The present experiments show that the medium used is a factor. Fluids which contain blood, or Albanese's solution, always produce stoppage in systole, whereas if Ringer's solution is employed as the medium, the stoppage is diastolic.   W. D. H.

Replacement of Urea in Artificial Solutions for the Isolated Heart of Selachians. R. BOMPIANI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 667—672).—Solutions containing urea, when administered by perfusion or otherwise, increase the time of survival of isolated hearts. The author's experiments on isolated hearts of *Torpedo ocellata* and *Scyllium* show that no substance will quite replace urea in this respect, but the derivatives of urea favour the survival more than other substances (methylcarbamide, survival 480 minutes; urea, survival 600 minutes), but the action is less marked the more distantly the substances are related to urea. Neither glycerol, acetone and urethane (although they are soluble in lipoids), nor the amino-acids, glycine, asparagine, aspartic acid and its salts keep the isolated hearts alive. R. V. S.

Toxicological Investigations on Bio-electric Currents. III. Comparative Toxicological Specificity of the Chemical Alteration Current, and Comparative Physiology and Toxicology of the Heart of Helix pomatia. C. LOVATT EVANS (*Zeitsch. Biol.*, 1912, **59**, 397—414).—Henze and Hermann have shown that skeletal and heart muscle of the frog responds specifically to poisons, and that the electrical changes run parallel to such action. This thesis is supported by the present investigations on the snail's heart, which is recommended as a convenient object for such work. Its electrogram is very simple, showing a pure diphasic effect, which corresponds with the single peristaltic wave which travels over it. Carbon dioxide acts tonically on it. The heart of the snail is sensitive to potassium, and very resistant to calcium; muscarine has the usual effect, but this is not antagonised by atropine. Antiarin has no action, but strophanthin and saponin are active. W. D. H.

Tolerance for Sugar in the Pig. ANTON J. CARLSON and F. M. DRENNAN (*J. Biol. Chem.*, 1913, **13**, 465—468).—Minkowski stated that the removal of the pancreas in the pig did not result in as severe diabetes as in other animals. In the present experiments, fatal diabetes did occur, but it was of slow onset. The pig has a lower tolerance for dextrose than any species so far studied; that is, it becomes glycosuric when quite small amounts of sugar are given by the mouth.

Occurrence of Metals in the Human Liver. LEOPOLD VAN ITALLIE and J. J. VAN ECK (*Pharm. Weekblad*, 1912, **49**, 1157—1163.* Compare Lehmann, A., 1896, ii, 486).—An investigation of the corpses of persons of various ages indicates that arsenic is not a normal constituent of the human liver, but that copper and zinc are always present, the proportion of copper being greater during the foetal period than in later life. Otherwise, age, sex, occupation, and place of residence appear to have no influence on the proportion of copper and zinc. The values given by Lehmann for the amount of copper present are appreciably too low. A. J. W.

* and *Arch. Pharm.*, 1913, **251**, 50—55.

The Influence of Iodine on Autolysis. M. KASCHIWABARA (*Zeitsch. physiol. Chem.*, 1912, **82**, 425—438).—Contrary to the statements of Kepınov (A., 1912, ii, 69), autolysis does not occur in a medium containing 0·5% of sodium hydroxide ; what does occur there is hydrolysis produced by the alkali ; this is only slightly increased by the presence of iodine. In alkali-free mixtures, iodine increases autolysis only in a slight degree. In rabbits which had received an intravenous injection of Lugol's solution, autolysis of the liver is also slightly accelerated, but even the fresh liver of such animals show an increase in non-coagulable nitrogen.   W. D. H.

The Catalytic Action of Iron Salts on the Autolysis of the Liver. LUIGI POLLINI (*Biochem. Zeitsch.*, 1912, **47**, 396—404).— Small and large quantities of ferric sulphate and ferric chloride increase the total nitrogen and the nitrogen of the monoamino-acids, proteoses and purine substances in the autolysis products when calves' liver is allowed to autolyse in the presence of these salts. Small quantities of iron citrate exert a weak inhibitory action, whereas larger quantities exert an accelerating action ; still larger quantities inhibit the autolysis as regards total nitrogen and the nitrogen of amino-acids. The proteose nitrogen, on the other hand, continually increases with increasing amounts of the iron salt. Very small quantities of iron lactate accelerate the autolysis, but progressingly larger quantities exert a progressive amount of inhibition.   S. B. S.

The Physiology of the Thyroid Glands. The Content of Phosphorus, Nitrogen, and Lipoids in the Organs of Thyroidectomised Animals. A. S. JUSCHTSCHENKO (*Biochem. Zeitsch*, 1913, **48**, 64—85).—The experiments were carried out with young dogs, of which a certain number were submitted to thyroidectomy, and an equal number from the same litter were used as controls. It was found that the organic and total phosphorus was diminished in the thyroidectomised animals in the brain, heart, and spleen, whereas the inorganic phosphorus is increased. In the liver, the changes were similar, but in the muscles the results were indefinite. In the kidneys the amount of phosphorus in all forms, and especially the inorganic, was increased. The nitrogen in the majority of the organs of thyroidectomised animals was increased ; this statement does not apply, however, to the kidneys and the serum. In animals with hyperthyroidism the total and organic phosphorus in brain, muscles, and heart are diminished ; in the liver, kidneys, spleen, and serum, on the other hand, they are increased. In most organs, the nitrogen content is diminished. In thyroidectomised animals, the lipoids, and all the fractions of the same, are diminished in quantity in the brain, liver, and muscles, whereas they are in increased amount in the serum. In other organs, the lipoid quantity is also less than in the normal. In hyperthyroidism, the content of lipoid in the serum is diminished, whereas no very definite results were obtained by the examination of other organs. The ratios of the nitrogen to phosphorus in various fractions of the lipoids in thyroidectomised animals, and in cases of hyperthyroidism, were also investigated. Thyroidectomy also

causes increase in the content of the purine substances of the organs. Complete thyroidectomy causes at first an increase in the phosphorus : nitrogen ratio in the urine, followed by a diminution of this ratio ; the quantity of urea diminishes. The quantity of ammonia at first falls, and then rises ; there is apparently an increase in amino-acids and purine bases; the creatinine, on the other hand, diminishes.

S. B. S.

Seasonal Variation in the Iodine Content of the Thyroid Gland. ATHERTON SEIDELL and FREDERIC FENGER (*J. Biol. Chem.*, 1913, 13, 517—526).—In sheep, ox, and pig there is about three times as much iodine in the thyroid between June and November as between December and May. In the sheep and ox (but not in the pig) the gland is larger during the latter months.   W. D. H.

Enzyme Synthesis. IV. Lactase of the Mammary Gland. HAROLD C. BRADLEY (*J. Biol. Chem.*, 1913, 13, 431—440).—These experiments give no support at all to the theory of enzyme syntheses in tissues, for lactase was never found in the mammary gland, or in the milk.   W. D. H.

Muscle Chemistry. IV. The Extractive Nitrogen and the Free Amino-nitrogen, Titratable by Formaldehyde in the Musculature of Different Animals. GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1912, 82, 439—462. Compare A., 1912, ii, 1077, 1078).—A large number of details of the distribution of nitrogen in muscle in many animals are given, and great variations are met with in both vertebrate and invertebrate animals ; but no constant and characteristic features distinguish the musculature of the various animal groups.   W. D. H.

Muscle Chemistry. V. Purine Bases of the Smooth Muscle of the Higher Animals. GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1913, 83, 45—49).—The purine bases of the smooth muscle of the ox (retractor penis) consist of oxypurines; xanthine, probably preformed, exceeds hypoxanthine in amount, which is the opposite to that found in striated muscle.   W. D. H.

The Formation of Lactic Acid in the Antiseptic Autolysis of Organs. NICOLAUS SOBOLEV (*Biochem. Zeitsch.*, 1912, 47, 367—373).—In estimating the lactic acid produced by autolysis of the organs, account was taken of the amount of acid carried down by the coagulum when the autolysis product was heated, the amount withdrawn from the solution in this process being estimated by Mondschein's method. At the ordinary temperature, less lactic acid is formed on autolysis than at 40°. Most organs show a maximum production at this temperature after about thirty-three days, after which the amount diminishes. The maximum production took place in the liver, followed by the spleen, heart, muscles, and kidneys in diminishing order.

S. B. S.

Enzyme Synthesis. II. Diastase and Glycogen of Animal Tissues. HAROLD C. BRADLEY and E. KELLERSBERGER (*J. Biol. Chem.*, 1913, 13, 419—424).—Tissues rich in diastase may or may not

contain glycogen, and what is more significant from the point of view of the enzyme-synthesis theory, tissues rich in glycogen may or may not contain diastase.   W. D. H.

Enzyme Synthesis. I. Lipase and Fat of Animal Tissues. HAROLD C. BRADLEY (*J. Biol. Chem.*, 1913, 13, 407—418).—No broad correlation exists between the amounts of fat and lipase in tissues. Some of the tissues which actively produce fat may, in fact, contain relatively little lipase, and tissues which are poor in fat may contain a good deal. The experiments afford no support to the theory of enzyme synthesis.   W. D. H.

The Influence of the Lipoids on the Action of Oxydases. HORACE M. VERNON (*Biochem. Zeitsch.*, 1912, 47, 374—395).—If minced tissue is left for half an hour in varying strengths of solu· tions of a narcotic up to a certain concentration, the narcotic is then washed out and the oxidising power of the tissue tested by a-naphthol and p-phenylenediamine, it will be found that the oxidising power is either uninfluenced or increased. In higher concentrations the oxydase is injured. Concentrations, twice or three times as large as those necessary to produce initial action, destroy the oxydase completely; thus, for example, acetone first in $4M$-solution attacks the oxydase, which is destroyed completely in $7M$-solution. These limits were investigated in several cases. The concentrations of monohydroxy-alcohols, which degrade the oxidative capacity 50%, are about twenty times stronger than those necessary to narcotise tadpoles, whereas in the case of fatty esters and methylurethane, they are twelve times stronger. In poisons other than lipoid-soluble substances, such as formaldehyde, the range of action is larger; thus, 1330 times as much formaldehyde is necessary completely to destroy the oxydase as is necessary to produce the initial action. In the case of the typical narcotic, paracetaldehyde, the relationship of these quantities is only 1·8:1. The range of action of ammonia is even greater than that of formaldehyde. Concentrations of narcotics which cause the initial effects are only a little greater than those necessary to hæmolyse red blood-corpuscles. The author draws the conclusion that the action of the indophenol oxydase is dependent on the lipoid, or perhaps the lipoid membrane, which, he considers, holds together the tissue oxydase and the peroxydase, which are thereby enabled to exert their joint action.   S. B. S.

The Ferments of the Purine Group. ARTHUR SCHULZ (*Biochem. Zeitsch.*, 1913, 48, 86—119).—In estimating uric acid in organs, formaldehyde up to 2% was added to the solution, after coagulating the proteins in the presence of sodium chloride and acetic acid. The effect of this addition is to render the uric acid more soluble. It was then estimated in the filtrate in the ordinary way by the Schmid-Krüger method. For investigating the uricolytic ferment, dried organ powders were generally employed. It was found that radium emanations of an activity of 5—10 Mache units per c.c were without any recognisable influence on the uricolytic action of

dogs' liver or ox-kidneys. Radium emanations increase the activity of the uricolytic ferments of ox-spleen, both as regards the formation of uric acid from added purine bases and from those produced by autolysis. The increased amount of uric acid formed varied, under the conditions of the experiments, from 10 to 20%. There was an increase, in the case of autolysis, in the activity of the proteolytic ferments, as shown by the increase in the nitrogen of the uncoagulable substances. This amount was, however, relatively less than the increased amount of uric acid formed. The uricolytic ferments of ox-kidneys are totally inhibited in action by fresh pulp of ox-spleen. Ox-kidney powder can inhibit the purine deamidases and the oxydases of the ox-spleen, but not the autolytic uric acid formation by the same organ. The author did not succeed in producing anti-uricolytic ferments by immunisation of rabbits by organs containing uricolytic ferments.   S. B. S.

Creatine, Creatinine, and Monoamino-acids in Certain Fishes, Mollusca, and Crustacea. Y. OKUDA (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, 5, 25—31).—Seven varieties of fishes were found to contain from 0·421 to 0·754% of creatine and 0·070 to 0·660% of creatinine. Mollusca contained only traces of these compounds, and crustacea only traces, if any at all.

All the marine animals examined contained much more nitrogen as organic bases than in the form of monoamino-acids, the amount of which is usually very small in fish, but somewhat higher in lobsters and cuttle-fish.

Most of the proteins are soluble in dilute alkali solution, and a good deal is soluble in 10% sodium chloride.   N. H. J. M.

The Occurrence of Glycogen in Sea-Molluscs (Especially Cephalopods and Aplysiæ). EMIL STARKENSTEIN and MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1912, 82, 417—424).—*Cephalopods* and *Aplysiae* have been stated to be free from glycogen. This is not so ; they contain abundance of it. Glycogen is the same substance whether it is derived from vertebrates or invertebrates.   W. D. H.

Carbon Metabolism. The Labile and Stable Carbon of the Urine. ENRICO REALE (*Biochem. Zeitsch.*, 1912, 47, 355—366).—The carbon of the urine was estimated by a wet-oxidation process, by oxidation with chromic acid and sulphuric acid, for which a modification of the apparatus of Desgrez (which is figured in the text) was employed. It was found that only about half the carbon in the urine exists in the form of urea. It was also found that a part of the carbon is readily oxidised to carbon dioxide in the presence of hydrogen peroxide when manganese peroxide is used as a catalyst. This is designated by the author "labile carbon," whereas the carbon which is not so oxidised is called "stable carbon." Full experimental details for the estimation of carbon in these two forms are given.   S. B. S.

The Intensity of Urinary Acidity in Normal and Pathological Conditions. LAWRENCE J. HENDERSON and WALTER W. PALMER (*J. Biol. Chem.*, 1913, 13, 393—405).—Normal urine ranges

from a concentration of ionised hydrogen of about 4·82 to 7·45 ; the mean value is 6·00. Pathological conditions occasionally cause a greater acidity, but never unusual alkalinity. No attempt is made at present to generalise, except in cises of cardio-renal disease, where the high mean acidity may indicate a form of acidosis.   W. D. H.

The Origin and Destiny of Cholesterol in the Animal Organism. X. The Excretion of Cholesterol in Man when Fed on Various Diets. GEORGE W. ELLIS and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1912, *B*, 86, 13—18. See A., 1912, ii, 275, 958).— In man as in other animals, the excretion of cholesterol in the fæces can be accounted for by that taken in with the food, provided the body-weight remains constant. If, however, a rapid loss of weight takes place, as in illness, the output of cholesterol exceeds the intake.

Further work will be necessary before this view can be regarded as established.   W. D. H.

Influence of Alkaline Salts in the Elimination of Urinary Ammonia by Normal Dogs. HENRI LABBÉ (*Compt. rend.*, 1912, 155, 1620—1622. Compare A., 1911, ii, 220).—With dogs in a state of nitrogenous equilibrium on a meat diet, the simultaneous ingestion of ammonium salts and excess of sodium carbonate produces a slightly less elevated elimination of volatile .basic nitrogen than when the ammonium salts are ingested alone. The difference is more marked with ammonium carbonate than with ammonium chloride. A large excess of sodium carbonate (about 2 grams per kilo. of body-weight), which provoked great thirst and marked polyuria, did not cause all the basic volatile nitrogen to disappear.   W. G.

The Relationship between the Nitrogen of the Amino-acids and Total Nitrogen in Urine under Various Normal and Pathological Conditions. ERNESTO SIGNORELLI (*Biochem. Zeitsch.*, 1912, 42, 482—506).—The experiments were carried out on dogs. The percentage of the amino-acid nitrogen (of the total nitrogen) varied in starvation between 1·09 and 1·30. It showed no very marked increase when oxidation was increased by the animals breathing pure oxygen. The value showed no marked differences when the proteins ingested by the animals were varied (caseinogen, gelatin, gluten, and zein). The percentage was only slightly increased (1·37—2·51) when the hydrolysis products of these proteins were administered subcutaneously. When azoturia was produced by fever, etc., the percentage still remained normal. In phosphorus poisoning, when the functions of the liver were disturbed, it rose to 3·66. Two hypotheses are advanced to account for the approximate constancy of the percentage : (*a*) that in all proteins there is a part which is not readily oxidised, and (*b*) that in the enzyme reaction producing deamidisation there is an equilibrium point at which part of the substance remains unacted on.   S. B. S.

The Fat Content of Normal and Pathological Urine. KŌZŌ SAKAGUCHI (*Biochem. Zeitsch.*, 1913, 48, 1—34).—The method

employed for estimating fat was that of Kakiuchi (A., 1910, ii, 549). The amount excreted in a normal adult urine is 0·0085 gram in twenty-four hours, which can be increased to 0·0341 gram after diets containing very large amounts of fat. Out of three cases of nephritis investigated, in only one was the fat excretion regularly above normal. In diabetes, tuberculosis of the lungs, jaundice, and cirrhosis of the liver, the excretion was normal. No extra excretion could be detected in cases of fractures of bones or re-section, and in this respect the results of the author differ from those obtained by earlier investigators.　　　　　　　　　　　　　　　　　　　　　S. B. S.

Urobilin. III. and IV. G. FROMHOLDT and N. NERSESSOV (*Chem. Zentr.*, 1912, ii, 1678; from *Zeitsch., expt. Path. Ther.*, 1912, 11, 400—407).—The administration of fresh bile leads to the appearance of urobilin in the urine, but this does not occur when pure bilirubin or bile extracted with ether is given. A method of extracting urobilin from blood is described. After preliminary extraction with alcohol and filtration, it is acidified and extracted with amyl alcohol, in which solvent the pigment is detected spectroscopically. If urobilin is absent from the urine, it is also absent from the blood, but when present in the urine it is usually present in the blood as well.　　　W. D. H.

Blood Destruction, Bile and Urobilin. The Formation of Bile Pigment in Blood. III. THEODOR BRUGSCH and KARL RETZLAFF (*Chem. Zentr.*, 1912, ii, 1678—1679; from *Zeitsch. expt. Path. Ther.*, 1912, 11, 508—525).—Estimations of urobilin in urine and fæces in various cases of liver disease lead to the conclusion that urobilinuria is the clinical expression for a series of substances related to blood and bile pigment. Hæmatogenous or extra-hepatic urobilin-uria occurs after extravasation of blood in the tissues; its other cause is usually hepatic insufficiency. If the bile enters the intestine, its pigment is converted into urobilin and re-absorbed; the liver then manifests its insufficiency by being incapable of re-synthesising bile-pigment from the urobilin, which therefore passes into the blood and urine. Urobilin in urine and fæces was estimated by making alkaline with ammonium carbonate and letting the mixture remain at 37° for two days. It was then extracted with light petroleum until Ehrlich's reaction was negative, then acidified with tartaric acid, and extracted with ether. A measured quantity of the ethereal solution was mixed with an ethereal solution of *p*-dimethylaminobenzaldehyde and a few drops of hydrochloric acid in absolute alcohol, and examined chromo-photometrically.　　　　　　　　　　　　　　　　　　　W. D. H.

The Protective and Curative Properties of Certain Food-stuffs against Polyneuritis Induced in Birds by a Diet of Polished Rice. EVELYN A. COOPER (*J. Hygiene*, 1913, 12, 436—462).—In pigeons weighing 350 grams, as much as 20 grams of raw beef are necessary daily to prevent polyneuritis; the anti-neuritic value of beef is therefore low. Heart muscle is better, and sheep's brain about twice as efficient as beef. Brain is specially efficient in preventing loss of body-weight which ensues when polished

rice is given. Fish is very inefficient in both directions. Egg-yolk, even if boiled, is the most efficient of all the animal foods examined : 3 grams daily is enough. Dried lentils and unhusked barley are about equal to egg-yolk. Yeast is the most efficient of all foods. The antineuritic and weight-maintaining action of the various foods differs. The weight-maintaining constituents are not protein, fatty or lipoidal. W. D. H.

Congenital Family Steatorrhœa. ARCHIBALD E. GARROD and W. H. HURTLEY (*Quart. J. Med.*, 1913, 6, 242—258).—The details of a curious case of an inborn metabolic error are recorded. The boy (aet. 8) has been subject since infancy to the passage of liquid fat from the bowel ; one cooling it solidifies ; another brother who died in infancy had the same defect. Health was apparently unaffected ; the stools contained 25% of the fat in the food ; with an intake of 177 grams of fat only 4% was split ; this figure rises when the intake is less, but even then it is not absorbed. Sodium glycocholate and various pancreatic preparations increased fat-splitting, but not the absorption ; indeed, the latter aggravated the condition. W. D. H.

The Mechanism of the Action of Silver Haloids. OSKAR GROS (*Arch. expt. Path. Pharm*, 1912, 70, 375—406).— Colloidal silver chloride and iodide intravenously injected in rabbits are strongly toxic, and the chloride is more so, even though the concentration of silver ions is the same in both cases. This is considered to be due to the formation of a complex of the silver salt and the chlorides of the blood plasma which is more readily carried to the tissue cells. Sodium iodide, which is non-toxic if given simultaneously, increases the poisonous action of silver iodide. This is explained on similar lines. In vitro, both salts are hæmolytic, and again the chloride is more effective, but here sodium iodide does not increase the action of silver iodide. W. D. H.

A Physiological Series of Cations. N. K. KOLTZOV (*Pflüger's Archiv*, 1912, 149, 327—363).—The observations were made on the effect of salt solutions on the vitality and contractility of a marine infusorian (*Zoothamnium alternans*). They follow in the main the work of Overton and others who have bestowed attention to osmotic phenomena and the rôle of the plasmatic membrane of cells. If chlorides are employed throughout, the cations are arranged in the following order : K, Rb, Na, Os, NH$_4$, Li, Sr, Mg, and Ca. Each member of the series lowers the surface tension of plasma-water less than the succeeding one, and toxicity runs parallel with the adsorption of the cations. W. D. H.

Temporary Fixation and Mode of Elimination of Manganese in the Rabbit. GABRIEL BERTRAND and FLORENTIN MEDIGRECEANU (*Compt. rend*, 1912, 155, 1556—1559).—Four rabbits received repeated subcutaneous injections of manganous sulphate in varying doses, and the effect on their weight and length of life was noted

Even with minute doses there was a marked loss in weight, and three injections of 5 mg. of manganese per kilo. of body-weight, at intervals of twenty-four hours, caused the death of the rabbit. The amount of manganese in the various organs of the four rabbits and of an uninjected rabbit was determined, and the results show that manganese, when subcutaneously injected, is rapidly diffused throughout the body, and all the tissues, including the nervous tissue, become temporarily impregnated. It is readily eliminated through the liver, bile, and mucus of the alimentary canal, and a small quantity is excreted in the urine. W. G.

The Action of Certain Substances of the Chloroform Group on the Vestibular Eye-Reflex. J. ROTHFELD (*Pflüger's Archiv*, 1913, 149, 435—446).—Nystagmus (vestibular eye-reflex) disappears under the influence of narcotics ; first vertical, then rotatory, and finally horizontal nystagmus. As anæsthesia passes off, they reappear in the reverse order. The substances employed in the research were chloroform, ether, chloral hydrate, and paracetaldehyde. The differences in detail between these four substances are treated at length. W. D. H.

The Fixation of Digitoxin (Merck) in the Organism of the Rabbit after Intravenous Injection. Comparative Experiments with Strophantin-*g*. CAMILL LHOTÁK VON LHOTA (*Biochem. Zeutsch.*, 1913, 48, 144—154).—If digitoxin is injected intravenously into rabbits, it disappears almost immediately from the blood (as ascertained by tests on the frog's heart), even when ten times the lethal dose is employed and the conditions of the animal are favourable. These conditions are, that the heart should be active, and the functions of the blood-vessels intact. If these are interfered with in any way (by narcosis, etc.), digitoxin can be detected in the blood when only twice the lethal dose has been employed. After injection of ten lethal doses, the digitoxin can be detected in all organs, especially the heart and liver. The greater the length of the circulatory system the drug must travel from the point of injection to reach the heart, the greater is the dose necessary to produce the specific action, This fact indicates that the drug is fixed by the vessels as well as the heart, and was demonstrated by experiments on animals with crossed circulatory systems. The drug can also be detected chemically at the point of application. Intravenously injected strophantin-*g* only disappears immediately from the blood in small quantities. S. B. S.

The Fate of Proline in the Animal Body. HENRY D. DAKIN (*J. Biol. Chem.*, 1913, 13, 513—516).—When proline is added to blood, and the mixture perfused through the surviving liver of a dog, there is no increase in the formation of acetoacetic acid ; but in the glycosuric animal it causes a marked increase in the sugar output. The formation of dextrose from proline involves the disruption of the ring. Glutamic acid also yields sugar (Lusk) ; so also do arginine and ornithine. The close structural relationship of glutamic acid, ornithine, and proline is shown graphically, W. D. H.

The Results of Poisoning with Adrenaline, Histamine, Pituitrin and Peptone in Relation to Anaphylaxis and the Vegetative Nervous System. ALFRED FRÖHLICH and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1912, '71, 23—61).—The substances mentioned in the title greatly lessen or abolish the excitability of the autonomic nervous system, both to faradic stimuli and to drugs. The same occurs in "peptone immunity" and in anti-anaphylaxis. As both these phenomena soon disappear, they are separable and reversible. The effect of the poisons is a selective one on the nerve endings. A considerable amount of the work recorded was performed on the uterus, and it was then found that after the use of histamine, adrenaline and pilocarpine had no effect, and pituitrin very little. After treatment with tyramine, pituitrin, histamine and adrenaline act normally; after treatment with pituitrin, adrenaline acts normally; after peptone, pituitrin, tyramine and adrenaline have no action. Barium chloride locally applied to the uterus causes contraction of the uterus after it has been rendered inexcitable by histamine, tyramine, or peptone.   W. D. H.

The Pharmacological Action of *p*-Hydroxyphenylethylamine. A. BICKEL and MICH. PAVLOV (*Biochem. Zeitsch*, 1912, 47, 345—354).—This substance, which can be isolated from ergot, shows the following actions. When 1—2 c.c. of a 0·5% solution are injected into rabbits or dogs of medium size, the arterial blood-pressure, after a short-lasting fall, rises, remains high for two or three minutes, and then sinks to normal. This is due to a contraction of the capillaries, with a consequent diminution of the amount of blood in the veins, which was detected by the measurement of the blood-flow in the venous system. As a further consequence there is a diminution of volume of organs which have a well-developed venous supply. This fact was demonstrated directly by the measurement of changes produced in the kidneys after the injection of the drug, and indirectly by the changes in the intestinal volume after injection of extracts of *Secale cornutum*.   S. B. S.

Action of Scopolamine (Hyoscine). ARTHUR R. CUSHNY (*Arch. expt. Path. Pharm.*, 1912, 70, 433—434).—A criticism on the work of Hug (A., 1912, ii, 790), who finds, like the author, that *l*- and *i*-hyoscine differ in their action on nerves. The quantitative differences between the two workers are explained as due to differences in the methods used.   W. D. H.

The Method of Action of Quinine. J. MOLDOVAN (*Biochem. Zeitsch.*, 1912, 47, 421—446).—The action on *Colpidia* is to cause a change in the state of the colloids of the protoplasm, leading to a separation of droplets of lipoid character, and producing a change in the osmotic relationship of the protoplasm to its surroundings; afterwards the nucleus and motility of the cell are injured, and finally death results. The cause of death is the stoppage of oxygen respiration. In the case of trypanosomes, the action is similar, but the separation of droplets is less marked, owing to the smaller content of lipoids. Similar actions were also observed on plant cells. There is a con-

siderable difference of behaviour in the individual cells as regards the resistance to the action of quinine, which depends on the energy of the oxygen respirations; older cells appear to be more resistant than young cells. The combined effect of two toxins on the cells is not the sum of the effect of each individual toxin, but depends, amongst other factors, on the relative concentrations of the two. In rabbits and guinea-pigs, the action of quinine is to diminish the oxidative processes, especially in the brain. This fact was demonstrated by various methods of intra vitam staining (according to the method of Ehrlich, etc.). The quinine in influencing the oxidative process does not effect the oxygen taken up, but acts as an anticatalyst. In view of the first action of quinine on cells, in causing the separation of the lipoids, it can act as a narcotic or local anæsthetic. To produce general narcosis, however, the required dose is so high that it acts deleteriously on the respiration, and it cannot therefore be used in practice for this purpose. S. B. S.

Influence of the Constitution of Purine Derivatives on their Action with Respect to Arterial Pressure. ALEXANDRE DESGREZ and DORLÉANS (*Compt. rend.*, 1913, 156, 93—94).—Whilst guanine on intravenous injection into a rabbit causes a diminution in the arterial blood pressure (compare A., 1912, ii, 585), hypoxanthine, xanthine, and uric acid exert a hypertensive action. The increase in pressure, whilst slight for hypoxanthine, is greater for xanthine and still greater for uric acid. From this it appears that the guanine owes its hypotensive action to the presence of the amino-group in its molecule. The action of these substances, especially of uric acid, is of interest in the pathogenesis of arthritic diseases, in which Bouchard has shown that there is marked arterial hypertension. W. G.

The Biological Action of Certain Protein Products Introduced Parenterally. ALFRED SCHITTENHELM and WOLFGANG WEICHARDT (*Chem. Zentr.*, 1912, ii, 1680; from *Zeitsch. Immunitätsforsch. exper. Ther.*, 1912, 14, 609—630).—The simple and conjugated proteins introduced into the blood stream are relatively innocuous; but the protein constituents of conjugated proteins (globin, histone, protamine) cause great depression of blood pressure, affect breathing and temperature, and lead in quite small doses to death. This has been attributed to the high percentage of diamino-acids they contain, but this cannot be the case because histone is poor in such acids, and certain kyrines rich in them are not toxic. Such proteins when united to nucleic acid or to hæmochromogen in the case of globin lose their toxicity. Toxic symptoms which occur when hæmolysis takes place in the blood stream may be due to the liberation of the poisonous globin (proteinogenous cachexia). W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Relation of Concentration of Food supply to the Generation Time of Bacteria. W. J. PENFOLD and (Mrs.) DOROTHY NORRIS (*J. Hygiene*, 1913, **12**, 527—531).—The generation time of *B. typhosus* in 1% peptone at 37° is forty minutes. If the peptone solution is less than 0·2% in strength the generation time is inversely proportional to the concentration. The addition of 0·17% of dextrose to a medium containing only 0·1% of peptone lowers the generation time by 50%; with 1% peptone this effect is less marked.

W. D. H.

The Bactericidal Properties of Blood Serum. I. The Reaction Velocity of the Germicidal Action of Normal Rabbit Serum on the Bacillus coli commune, and the Influence of Temperature Thereon. (Miss) HARRIETTE CHICK (*J. Hygiene*, 1913, **12**, 414—535).—The action *in vitro* of rabbit serum on *B. coli* consists of several phases, the duration of which is inversely proportional to temperature. Its germicidal action follows the logarithmic law, and so falls into line with other cases of disinfection. Its temperature-coefficient is low (2·84 to 1·93).

W. D. H.

Chemical Action of Bacillus cloacæ (Jordan) on Citric and Malic Acids. JAMES THOMPSON (*Proc. Roy. Soc.*, 1912, *B*, **86**, 1—12).—The respiratory coefficient for malic and citric acids was determined and found to be 1·63 and 2·35—3·2 respectively.

In the presence of oxygen, *B. cloacæ* decomposes malic acid with the production of carbon dioxide, acetic acid, succinic acid, a small quantity of fatty substance, and traces of alcohol. It is suggested that the action probably goes on in two ways: an oxidation of acid to carbon dioxide and acetic acid by atmospheric oxygen, and an oxidation accompanied by reduction of a portion of the acid to succinic acid. The organism does not attack malic acid in the absence of oxygen.

The products resulting from the decomposition of citric acid are the same as from malic acid. Under aerobic conditions the amount of acetic acid is greater, whilst anaerobic conditions lead to an increase in the production of acetic and formic acids. Acetylmethylcarbinol is not formed by the action of *B. cloacæ* on malic or citric acids.

H. B. H.

The Degradation of Polypeptides by Bacteria. II. The Action of the Non-liquefying Organisms TAKAOKI SASAKI (*Biochem. Zeitsch.*, 1912, **42**, 462—471. Compare A., 1912, ii, 669).—Organisms which are incapable of liquefying gelatin contain nevertheless an erepsin-like ferment capable of hydrolysing glycyl-glycine and glycyl-*l*-tyrosine. Relatively large quantities of tyrosine could be isolated as a result of the action. This action was demonstrated

by typhus and various strains of paratyphus bacilli, various bacilli of dysentery, bacilli of mouse typhus, chicken cholera, a id *Micrococcus*

S. B. S.

The Degradation of Polypeptides by Bacteria. III. The Action of Liquefying Organisms. TAKAOKI SASAKI (*Biochem. Zeitsch.*, 1912, **47**, 472—481).—Glycyl-glycine and glycyl-*l*-tyrosine were hydrolysed (in Fränkel's solution) by the following strains. Bacilli of splenic fever, *Staphylococcus pyogenes aureus, citreus,* and *albus, B. subtilis, B. proteus vulgaris, B. pyocyaneus, B. prodigiosus,* cholera vibrio, and the vibrios of Metchnikov and Dunbar and the water vibrio.

S. B. S.

Production of Citric Acid from Glycerol by Fungi. CARL WEHMER (*Chem. Zeit.*, 1913, **37**, 38—39. Compare A., 1893, ii, 591; 1909, ii, 602; 1910, ii, 60, 61).—When two species of *Citromyces* were grown in nutrient solution containing ammonium nitrate, potassium phosphate, magnesium sulphate, calcium carbonate, and glycerol (3—20%), large quantities of citric acid were produced. In the absence of calcium carbonate no such accumulation occurs, and it is assumed that, in the absence of any neutralisable base, any citric acid formed is destroyed immediately by the fungi. Similar growth takes place when the glycerol is replaced by sucrose, lactose, mannitol, xylose or arabinose. Sucrose is inverted, and reducing substances are formed in cultures supplied with glycerol. The author discusses the mechanism of citric acid formation from glycerol, and contests the view advanced by Mazé, that acid is only produced when there is a deficiency of nitrogen, or that it is in any way due to a lack of iron or zinc.

H. B. H.

Action of Hydrogen Ions, Boric Acid, Copper, Manganese, Zinc, and Rubidium on the Metabolism of Aspergillus niger. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 753—764).—In investigating the culture conditions of *Aspergillus niger* it is not sufficient to merely ascertain the dry weight produced, as was done by Raulin and others. Spore formation, for instance, produces differences in composition. It is, therefore, desirable to determine the changes of the plastic equivalent, or of the assimilation quotient, several times during development.

Addition of 2·35 c.c. of *N*-sulphuric acid to 100 c.c. of culture solution and of 0·5% of boric acid has very slight effect on the plastic equivalent of the carbon.

A high weight of mycelium is not always a favourable indication. It was found that certain concentrations of copper sulphate, zinc chloride and sulphate considerably increase the plastic equivalent of the carbon, whilst the increase in the weight of mould is proportional to the retarded spore production. Very dilute zinc solutions have no effect; copper salts, in all dilutions, counteract spore formation. Minimal quantities of manganese do not alter the plastic equivalent of the carbon, but only affect the rate of metabolism. The amounts of dry matter found by Bertrand should be considered as values indicating the velocity of the process.

When potassium is replaced by rubidium, spore formation is checked, the weight of mould increased, whilst the metabolism of the carbon remains the same.   N. H. J. M.

Influence of Zinc, Magnesium, Calcium, Potassium, and Sodium Salts on the Growth of Aspergillus niger. J. BUROM-SKI (*Centr. Bakt. Par.*, 1912, ii, 36, 54—66. Compare A., 1908, ii, 124 ; 1911, ii, 222, 421, 664 ; 1912, ii, 377, 861).—The fungus was grown in a medium consisting of ammonium sulphate or nitrate 1%, sucrose 5%, magnesium sulphate 0·25%, monopotassium phosphate 0·5%, traces of ferrous sulphate, and distilled water. The addition of zinc sulphate in the proportion of 0·001—0·1% led to an increase in the respiratory coefficient (car bon dioxide crop) : that of the control and treated cultures respectively being 1·8 and 2·4 at 30°, and 2·8 and 3·5 at 20°. The addition of calcium sulphate to magnesium-free medium decreased the growth of the organism ; 0·25% magnesium sulphate to magnesium-free medium increased the crop very greatly, whilst calcium and magnesium sulphates increased the growth still more. The presence of calcium salts prevents the accumulation of oxalates in the cultures. Magnesium sulphate may be beneficially increased to 0·5%, although fructification begins to be affected at this concentration. Sodium salts proved to be without value, but increasing amounts of potassium salts caused corresponding increases of growth. Magnesium and potassium salts therefore, not only serve as nutrients, but also exercise a stimulative action.   H. B. H.

Enzymatic Nature of Uric Acid and Hippuric Acid Ferment-ation. ALEXANDER KOSSOWICZ (*Chem. Zentr.*, 1912, ii, 1300, 1482 ; from *Zeitsch. Gährungsphysiol*, 1, 121—123, 317—319. Compare this vol., i, 146).—Filtered solutions from cultures of *Aspergillus niger*, *Mucor Boidin*, *Phytophthora infestans*, *Isaria farinosa*, and *Botrytis bassiana*, in which urea was present as only source of nitrogen, liberated ammonia from uric and hippuric acid, and from the latter, benzoic acid as well. A filtrate from *Cladosporium herbarum* only showed distinct production of ammonia in the case of uric acid. Similar results were obtained by means of the alcohol precipitates obtained from the filtrates from *Aspergillus* and *Cladosporium*.

Referring to Shibata's negative results with *Aspergillus niger* and uric acid, it was found in similar experiments that *Aspergillus niger*, *Mucor Boidin*, *Phytophthora infestans*, *Isaria farinosa*, *Botrytis bassiana*, and *Cladosporium herbarum* all produce ammonia from uric acid, and that all, except *Cladosporium*, decompose hippuric acid with production of ammonia and benzoic acid.   N. H. J. M.

The Rate of Fermentation as Measured by Difference of Potential. M. C. POTTER (*Proc. Univ. Durham Phil. Soc.*, 1912, 4, 230—231. Compare *ibid.*, 1910, 3).—It has been shown previously that during the fermentation of sugar by yeast an $E.M.F.$ is developed. The author now finds that the measurement of the rate of fermentation by the development of the $E.M.F.$ and by the evolution of carbon dioxide as in Slator's method are in close agreement, so that the electrical method provides a ready means of determining the rate of fermentation.

Experiments are also quoted, showing that the carbon dioxide given off during fermentation carries an electric charge, and that the rate of fermentation is uninfluenced by the potential of the fermenting liquid.

F. B.

Fermentations with Yeast in the Absence of Sugar. IX. Fermentation of Keto-acids by Wine Yeasts. CARL NEUBERG and J. KERB (*Biochem. Zeitsch.*, 1912, 47, 405—412).—Wine yeasts, of which a large number of German varieties were investigated, exert the same action on pyruvic acid as the beer yeasts, giving rise to acetaldehyde (which was isolated as its *p*-nitrophenylhydrazone) and carbon dioxide. These yeasts also attack oxalacetic acid and *a*-keto-*n*-butyric acid.

S. B. S.

Fermentations with Yeast in the Absence of Sugar. X. The Fermentation of *a*-Ketobutyric Acid CARL NEUBERG and J. KERB (*Biochem. Zeitsch.*, 1912, 47, 413—420).—This acid is very readily attacked by various yeasts and yeast preparations. The actual course of fermentation is not yet ascertained, in that propaldehyde could only be isolated in small quantity (about 4%). *a*-Ketoglutaric acid is also very readily attacked; phenylpyruvic acid is also fermented, but not *ay*-diketovaleric acid.

S. B. S.

The Acidification of Musts by Yeasts during Alcoholic Fermentation. AUGUSTE FERNBACH (*Compt. rend.*, 1913, 156, 77—79). A study of the influence of the original acidity of the medium on the production of acids during the fermentation by yeasts of a saccharine liquid. Even in varying conditions the results show that the acidification produced by the yeasts, independently of their individual character, is subject to the acidity of the medium in which they function, low acidity in the medium favouring high acid production.

W. G.

Fixation of Elementary Nitrogen by Yeasts, Monilia candida, and Oidium lactis. ALEXANDER KOSSOWICZ (*Bied. Zentr.*, 1913, 42, 68—69; from *Zeitsch. Gährungsphysiol*, 1).—The results of experiments with (1) *Saccharomyces Pastorianus III Hausen*; (2) *Monilia candida*; (3) *Saccharomyces membranaefaciens*; (4) *Saccharomyces anomalus*; (5) *Oidium lactis*, cultivated in solutions containing sucrose (5%), glucose (0·2%), and mannitol (0·2%), in addition to minerals, showed in three months the following gains of nitrogen: (1) 4·8 and 5·2; (2) 6·2 and 6·8; (3) 6·9; (4) 7·4, and (5) 4·8 and 5·8 mg.

The air in the flasks was freed from combined nitrogen.

N. H. J. M.

Mode of Action of Dilute Solutions of Electrolytes on Germination. HENRI MICHEELS (*Bull. Acad. roy. Belg.*, 1912, 753—765. Compare A., 1910, ii, 883).—Germination experiments with wheat in electrolysed and non-electrolysed *N*/100-potassium chloride solutions through which chlorine was passed showed that chlorine was rendered more favourable by the cathode liquid and was poisonous in the non-electrolysed solution.

In the case of potassium hydroxide (25 c.c. of a 0·1% solution added to 500 c.c. of N/100-potassium chloride), a very injurious effect was observed in the non-electrolysed solution; its toxicity was diminished in the anodic liquid, but only in a slight degree.

Copper sulphate (N/200) in anodic solution, which is acid, is more toxic than the cathodic solution, which is only slightly acid. The solution is toxic when not electrolysed.

Comparing N/100-potassium chloride with electrolysed solutions in which the cathodic and anodic liquids received hydrochloric acid and potassium hydroxide respectively, the best results were obtained in the non-electrolysed solution and in the cathodic liquid notwithstanding the acidity, whilst the disappearance of the acidity of the anodic liquid only slightly diminished its toxicity.

The conclusion is drawn that anodic and cathodic liquids owe their characters in part to the liberated cations and anions, not passed to the chemical state. In solutions of electrolytes, the action of cations would not be exclusive, but only preponderating.   N. H. J. M.

Effects of Manurial Salts on the Germination of Different Plants. ALBERT RUSCHE (*J. Landw.*, 1912, 60, 305—365; from *Diss.*, Göttingen, 1912) —Potassium chloride does not act unfavourably on the germination of cereals, peas, rape, and beet, but is unfavourable in the case of clovers, serradella, lucerne, and lupins, especially white clover and serradella. Sodium chloride is more unfavourable than potassium chloride, except with barley, lupins, serradella, and rape. Magnesium and calcium chlorides generally have the same effect as potassium chloride, but not in every case; whilst ammonium chloride is injurious, especially with clovers. Nitrates are generally more favourable than chlorides; ammonium nitrate, however, resembles the chloride. Potassium sulphate is generally favourable, except with serradella; sodium sulphate is similar in its effects, whilst magnesium and calcium sulphates are also favourable. Of all the salts employed, sodium and potassium carbonates are the most favourable.

As regards the length of roots, nitrates produced the shortest roots with cereals. The longest roots were obtained with sulphates and phosphates.

In the case of peas the longest roots were obtained when no manure was employed. With red clover the longest roots were produced under the influence of sulphates and carbonates, the shortest with carbonates and chlorides.

The full results relating to germination, length and weight of roots, and the development of the above-ground parts of the different plants are given in numerous tables.   N. H. J. M.

Influence of Previous Conditions on the Value of the Respiratory Quotient of Green Leaves. LÉON MAQUENNE and EM. DEMOUSSY (*Compt. rend.*, 1912, 156, 28—34).—The authors have studied a number of abnormal cases where the respiratory quotient of leaves gathered in full sunlight was considerably lower than that of leaves which had been kept in the dark for several hours. They worked with leaves of sorrel, stonecrop, geranium, rhubarb, and *Sedum*

acre, and from their results they consider that the respiration of a plant is effected in two successive phases ; the first leading to a production of fixed acids, the result of an oxidation rendered incomplete owing to the slowness of penetration of the oxygen ; the second to a combustion of these acids.   It is necessary also to take into account the solution of the carbon dioxide in the cell-sap and the temperature, which has an influence both on the acidification and the absorption of carbon dioxide by the leaf.

Working with an *Aspidistra* leaf and observing the variation of pressure, using their manometric measuring apparatus (compare A., 1912, ii, 1201), they find that with leaves taken straight from the sunlight the pressure at first diminishes and then rises, whilst with leaves kept in the dark for some hours before measuring, the pressure rises immediately and continuously.   W. G.

Hydrolysis and Displacement by Water by Nitrogenous and Mineral Substances Contained in Leaves. GUSTAVE ANDRÉ (*Compt. rend.*, 1912, 155, 1528—1531. Compare A., 1912, ii, 198).—Chestnut leaves show much the same loss of nitrogen, phosphoric acid, and potassium, by exosmosis, when steeped in water, as do grains of wheat and haricot beans (compare A., 1912, ii, 591). After 255 days steeping, the leaves had lost 6·27% of their nitrogen, 74·14% of phosphoric acid, and 94·58% of potassium. Most of the loss occurred in the first few days, and it was found to be more rapid the younger were the leaves.   W. G.

Does Potassium Participate in the Building Up and Degradation of Carbohydrates in Higher Plants ? JULIUS STOKLASA and E. SENFT (*Zeitsch. landw. vers. Oesterr.*, 1912, 15, 711—736) —It is found that by the action of ultraviolet rays on nascent carbon dioxide and hydrogen in the presence of potassium hydroxide a photosynthesis occurs with the formation of formaldehyde, and that the latter subsequently condenses to furnish sugars ; the reduction of carbon dioxide in the cell does not take place in the absence of potassium hydrogen carbonate, even in the presence of nascent hydrogen ; and formic acid (which is subsequently reduced) is also found to be one of the products of this reaction.   F. M. G. M.

Enzyme Synthesis.   III.   Diastase and Starch of Plant Tissues. HAROLD C. BRADLEY and E. KELLERSBERGER (*J. Biol. Chem.*, 1913, 13, 425—430).—With some exceptions the results in this series are more favourable to the view of enzyme synthesis in the tissues, for no tissues which contain starch are destitute of diastase, although many tissues which contain diastase are free from starch.
                                                                   W. D. H.

Occurrence of Arsenic in the Vegetable Kingdom. F. JADIN and A. ASTRUC (*J. Pharm. Chim.*, 1912, [vii], 6, 529—535).—The occurrence of arsenic in the vegetable kingdom appears to be general, as the authors have detected its presence in some sixty-seven different kinds of vegetables, fruits, cereals, plants, parasitic plants, fungi, etc.

The quantity of arsenic found per 100 grams of substance varied from 0·008 mg. in dates to 0·266 mg. in radishes. Parasitic plants contained arsenic, even although they were not in direct contact with the soil, but there was no relation between the amounts of arsenic in the parasite and its support. Plants belonging to the same family do not invariably contain similar quantities of arsenic, but in the case of one and the same plant the portions containing chlorophyll contained more arsenic than the parts not exposed to light. It is pointed out that one of the sources of the arsenic found in animal organs lies in the vegetable substances consumed as food.   W. P. S.

Stimulative Action of Manganese and Copper Sulphates on Plants. L. Montemartini (*Bied. Zentr.*, 1913, **42**, 65; from *Staz. sper. agrar. ital.*, 1911, **41**, 564).—Manganese and copper sulphates absorbed from aqueous solutions stimulate respiration, the effect varying with different plants. Vine plants are stimulated by 0·001% manganese sulphate, whilst greater concentrations are injurious, and are injured by 0·01% of copper sulphate. Garden beans, and still more potatoes leaves, are more resistant and more stimulated.   N. H. J. M.

Demonstration of Carotinoids in Plants. Separation in Crystalline Form. C. van Wisselingh (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 511—526).—The various methods employed in detecting the presence of carotinoids are described. Indications were obtained that several distinct carotinoids frequently occur in plants.   N. H. J. M.

Demonstration of Carotinoids in Plants. Behaviour of Carotinoids towards Reagents and Solvents. C. van Wisselingh (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 686—692).—In presence of carotinoids a blue coloration is produced by strong sulphuric, sulphurous, and nitric acids, bromine water, and strong hydrochloric acid with a little phenol or thymol; iodine dissolved in potassium iodide solution or chloral hydrate gives a green coloration. Two new reagents were also employed: concentrated solutions of antimony trichloride and of zinc chloride, both in 25% hydrochloric acid, which colour crystals of caratinoids dark blue.

Lists of flowers and other parts of plants which were tested with the different reagents are given.   N. H. J. N.

Demonstration of Carotinoids in Plants. Leaf of Urtica dioica, the Flower of Dendrobium thyrsiflorum and Hæmatococcus pluvialis. C. von Wisselingh (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 693—700)·—The flower of *Dendrobium thyrsiflorum* contains two carotinoids, one of which, of a reddish-orange colour, is not common in plants, and perhaps belongs to the xanthophylls. The examination of *Haematococcus pluvialis* indicated the presence of a greater number of carotinoids than have hitherto been detected (compare Zopf, *Biol. Centr.*, 1895, **15**, 417; H. C. Jacobson, *Folia Microbiol*, 1912, **1**, 24).   N. H. J. M.

Mannitol in the Sap of Asparagus.   E. Busolt (*J. Landw.*, 1912, 60, 393—396).—The mannitol in the sap of asparagus is produced by fermentation, and is not originally present.

N. H. J. M.

Presence of Stachyose in the Haricot and in the Seeds of Some Other Leguminoseæ.   Georges Tanret (*Compt. rend.*, 1912, 155, 1526—1528).—The author has isolated stachyose in a crystalline form, by means of its strontium compound, from the haricot bean and the seeds of certain other leguminoseæ, namely, lentils, clover, galega, lupin, and the soja bean.   In all cases sucrose was present as well.   The lupeose, obtained as an uncrystallisable syrup from haricots and lupins by Schulze, was, therefore, stachyose in an impure state.   No stachyose could be isolated from pea-seeds.

W. G.

Presence of Adenine and Aspartic Acid in Mulberry Leaves.   Z. Mimuroto (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, 5, 63—65).—From 500 grams of air-dried mulberry leaves, 1·2 gram of adenine (as picrate) and 0·3 gram of aspartic acid were obtained.

N. H. J. M.

Action of Stimulants on Rice.   Manuel Rocas (*Bied. Zentr.*, 1913, 42, 41—42; from *Philippine Agric. Forester*, 1912, 1, 89).— Previous investigations indicate that there are no poisons which cannot act as stimulants on plants ; that compounds of gold, silver, platinum, mercury, tungsten, palladium, copper, nickel, cobalt, boron, tin, cadmium, tellurium, arsenic, iodine and fluorine are poisonous, whilst chromium, manganese, bismuth, sulphur and magnesium are only poisonous under certain conditions.

The following concentrations of the various compounds were found to be favourable : sodium borate, 1/1000 ; manganese sulphate, 1/1000; ferrous sulphate, 1/1000 ; ferric chloride, 1/5000 ; copper sulphate, 1/2000 ; nickel sulphate, 1/5000 ; cobalt nitrate, 1/10,000, and zinc sulphate, 1/1000 mol. solutions.

Mercuric chloride in 1/50,000 mol. solutions inhibited growth, whilst ferric chloride and copper sulphate (1/1000) are injurious, and sodium borate (1/100) somewhat injurious.

The optimum results for rice are generally much higher than previous experiments have shown for other plants.   The experiments were, however, not made with water-cultures, but in soil.   N. H. J. M.

Presence of Nicotinic Acid in Rice Bran.   Umetaro Suzuki and S. Matsunaga (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, 5, 59—61). —Nicotinic acid was obtained from rice bran, freed from fat, by extracting with 80—85% alcohol.   The acid had not previously been found in any vegetable substance.   The yield of picrate amounted to about 1 gram from 1 kilo. of bran.   N. H. J. M.

The Substitution of Different Chemical Elements for Zinc in the Culture of Sterigmatocystis nigra.   Maurice Javillier (*Compt. rend.*, 1912, 155, 1551—1552).—The author has

replaced the zinc in the culture medium of *Sterigmatocystis nigra* by a wide range of other elements, and, with the exception of one, namely, cadmium, they were all without influence on the crop. While the addition of zinc to the extent of 1 in 10,000,000 produces a crop 6·2 times as great as in its absence, the same concentration of cadmium produces a crop only 2·6 times as great, and cadmium has a marked injurious effect on the sporulation.   W. G.

Volatile Aliphatic Acids of Corn Silage. ARTHUR W. Dox and RAY E. NEIDIG (*J. Amer. Chem. Soc.*, 1913, 35, 90—93).—With reference to the work of Hart and Willaman (Abstr., 1912, ii, 1205) on the volatile fatty acids and alcohols in maize silage, the authors draw attention to their own paper on the subject (*Iowa Agric. Exp. Sta., Research Bull.*, 1912, 7, 32). The results are in fair agreement, except with regard to formic acid and methyl alcohol; in the latter investigation, only traces of formic acid were found and methyl alcohol was absent, whereas Hart and Willaman found 17% of formic acid in the volatile acids and 21% of methyl alcohol in the alcohols. Certain sources of error are pointed out in the methods employed by Hart and Willaman, and it is considered that these may account for the discrepancies.   E. G.

Action of Long-continued Exclusive Manuring on Plants and Soils. S. GRAF ROSTWOROWSKI (*J. Landw.*, 1912, 60, 371—392). —The results of experiments with potatoes showed that, when there is a tendency to leaf curl, it is desirable to employ potassium salts in moderation.

As regards the effect of manures on the composition of potato ash it was found that the ashes of potatoes from plots manured with potassium and with potassium + phosphorus + nitrogen were almost identical in composition, and there was also no difference between the ashes of potatoes from plots manured with nitrogen and the unmanured plot.

The composition of the ash of potato leaves varied considerably with different manures; potash varied from 5% (unmanured) to 33% (potassium manure), and lime varied from 21% (potassium alone, or with phosphorus and nitrogen) to 41% (unmanured). Application of sodium nitrate resulted in a high percentage of sodium in the leaf ash.

Notwithstanding the long-continued application of potassium manures, the potash in the ash of the tubers never reached 60%.

Experiments were also made to ascertain the effect of the long-continued manuring on the soil.   N. H. J. M.

Chemical and Physical Nature of "Roterden." EDWIN BLANCK (*J. Landw.*, 1912, 60, 397—400).—A reply to Hissink (A., 1912, ii, 981; compare van der Leeden and Schneider, *Internat. Mitt. Bodenkunde*, 1912, 2, 81).   N. H. J. M.

Analysis of a Florida Clay. ARCHIBALD A. HALL (*Proc. Univ. Durham Phil. Soc.*, 1912, 4, 228—229).—The author gives an analysis of a clay subsoil underlying peat, from Duval in the great swamp of Florida, and points out that the composition of this clay, on which

vegetation is now growing under conditions which approximate to those of the coal age, is very similar to that of a typical underclay, underlying coal.   F. B.

Osmosis in Soils.   Soils Act as Semipermeable Membranes.   I.   C. J. LYNDE (*J. Physical Chem.*, 1912, 16, 759—765).— The movements of water in soil have been attributed to gravitation, capillary action, and heat. To these must now be added osmotic pressure.

Osmotic cells of the Pfeffer type were prepared as follows: Glass tubes 150 mm. × 11 mm. diameter were closed at one end with cotton cloth and wire gauze. A layer of sterilised heavy clay subsoil was deposited in each tube, and consolidated against the cloth by centrifugal action. The tubes were filled up with 10% sugar solution, or 10% potassium sulphate solution, and immersed in distilled water. In each case water diffused into the cells osmotically through the clay. The rate of diffusion inwards was considerably greater at 24·5° than at 22·5°. It is probable that the solution leak outwards through the clay was considerable.   R. J. C.

Osmosis in Soils.   Soils Act as Semipermeable Membranes. II.   C. J. LYNDE and F. W. BATES (*J. Physical Chem.*, 1912, 16, 766—781. Compare preceding abstract).—Three pairs of osmotic cells were prepared with clay subsoil as already described, the layers of sterilised clay being 54 mm., 36 mm., and 18 mm. thick respectively. The solution filling the cell was the aqueous extract of the clay forming the membrane in each case. The cells were closed by rubber stoppers carrying capillary tubes. The predetermined capillary rise of each solution was deducted from the total rise, the remainder being the osmotic rise.

The osmotic pressures obtained with the thickest layers of clay were the highest, but the concentrations of the soil solutions were also highest in these cases. On the assumption that the osmotic pressures should be equal to these given by solutions of potassium chloride of equal electrical conductivity, the osmotic efficiency of the membranes was calculated to be only 2·5% (54 mm. membrane), 1·4% (36 mm.), and 1·0% (18 mm.), the efficiency being roughly proportional to the thickness of the membrane. An experiment with a membrane of clay 108 mm. thick gave still higher pressures. It is calculated that about 2 metres thickness of clay would be a perfect semipermeable membrane. In all cases the osmotic rise at 36·5° was somewhat higher than at 16·7°.

The soil used in the above experiments had the physical composition: sand 10·5%, silt 50·4%, clay 36·3%, organic matter 2·8%. A number of soils containing 44—61% of sand and only 12—16% of clay failed to show any decided osmotic properties.

It is suggested that osmotic effects play an important part in agricultural operations, particularly on heavy clay subsoils. Tillage, drainage, manuring, and mulching by favouring bacterial action increase the proportion of soluble matter in the soil, and therefore the amount of moisture which is raised osmotically through the subsoil. The same

effect may be brought about by the addition of mineral fertilisers and such substances as gypsum and salt which are not directly plant foods. There may be other substances which are not plant foods, but might be beneficial as fertilisers from the osmotic point of view.   R. J. C.

Importance of the Error of Analysis in Questions Relating to the Nitrogen Economy of Arable Soils. THEODOR PFEIFFER and EDWIN BLANCK (*Landw. Versuchs-Stat.*, 1912, **78**, 367—374).—A final attempt was made to obtain a satisfactory nitrogen balance with the experimental soils at Breslau. Six plots (9 sq. metres each) were selected, which had given similar amounts of crops during two years, and from each plot five samples of soil were taken. Ten or twelve nitrogen estimations were made with each sample. The experimental error was found to be ±0·00086, which would correspond with 25·8 kilos. of nitrogen per hectare to a depth of 25 cm. if the weight of the soil is taken as 3,000,000 kilos., or 32·2 kilos. if the total weight of soil is taken as 3,750,000 kilos. As this number has to be multiplied by three it would only be possible to show a difference exceeding 77·4 or 96·6 kilos. of nitrogen per hectare. With fewer samples or analyses the error would, of course, be greater. It must also be borne in mind that the nitrogen of crops is not all derived from the surface soil, but from the subsoil as well.   N. H. J. M.

Estimation of the Value of Plant Foods in Soils and Manures so far as Dependent on Solubility. J. G. MASCHHAUPT and L. R. SINNIGE (*Bied. Zentr.*, 1913, **42**, 16—20; from *Verslag. Landbouwkund. onderzoek. Rijkslandbouwproefstat.*, 1912, No. 11).— Single extractions of different phosphates with a definite volume of water containing carbon dioxide will not show the relative values of the manures. Better results will be obtained when successive extracts are made, and it is probable that a method of continuous extraction in which the dissolved substances are at once removed will give better results than intermittent extraction.

Repeated extraction with fresh amounts of citric acid solution will probably indicate the relative values of phosphates. As, however, carbon dioxide is the chief solvent at the disposal of soil and roots, it is to be preferred to citric acid.   N. H. J. M.

Antagonism between Anions as Affecting Ammonification in Soils. CHARLES B. LIPMAN (*Centr. Bakt. Par.*, 1913, ii, **36**, 382—394).—Experiments in soils on the lowering of the toxicity of salts by the addition of other salts, as measured by the amount of ammonia produced. The first series, which deals with the antagonism between the salts of "white alkali," sodium chloride and sulphate, showed that addition of sodium chloride (0·2%) to the soil reduced the amount of ammonia from 54·46 to 30·73 mg., whilst the further addition of sodium sulphate (0·3%) increased the amount to 37·1 mg., less effect being produced by smaller or larger amounts of sulphate. In an experiment with sodium chloride and carbonate, the ammonia was reduced from 41·75 to 22·05 mg. by 0·2% of sodium chloride; sodium carbonate in amounts of 0·2% and more increased the ammonia

production, the greatest amount being 70·7 mg. with 0·7% of sodium carbonate in addition to 0·2% of chloride.

Further experiments are described in which sodium sulphate and carbonate were employed.

The results show that antagonism is shown most strongly between sodium carbonate and sodium chloride ; next between sodium carbonate and sodium sulphate, and least between sodium chloride and sodium sulphate.

When 0·3 or 0·4% of sodium carbonate is added to soil containing 0·9% of sodium sulphate there is an increased toxic effect ; when, however, the amount of carbonate is increased to 0·5%, the toxic effect of the sulphate is reduced, and with 0·6% of carbonate it is still further reduced.   N. H. J. M.

Influence of Organic Substances on the Decomposition and [Manurial] Action of Nitrogenous Compounds. MAX GERLACH and ALFRED DENSCH (*Bied. Zentr.*, 1913, 42, 21—30 ; from *Mitt. Inst. Landw. Bromberg*, 1912, 4, 259).—Pot experiments in which slightly humus, loamy sand manured with sodium nitrate both alone and with dextrose and straw respectively ; with an ammonium salt, alone and with dextrose ; and with dextrose and straw respectively, was kept for two months, after which the amounts of total nitrogen and the nitrates and soluble organic nitrogen were estimated.   The results showed that the total nitrogen changed very little, and indicated that the nitrogen added as ammonium salt and as nitrate was converted into insoluble proteins.

The same soil was then utilised for a series of vegetation experiments from April, 1909, to August, 1911, during which time, oats, mustard, rye, mustard and wheat were grown.

Dextrose and straw was always unfavourable to oats, but were beneficial to next plants (mustard).   The final results relating to nitrogen did not show any greater increase when dextrose was added than without.   Nitrogen applied as nitrate showed no loss, whilst application as ammonium sulphate resulted both in loss and gain. Straw alone and in conjunction with nitrate had only a slight effect on the total nitrogen.

The results indicate that ammonium salts and nitrates are converted into insoluble proteins in presence of undecomposed organic substances, and that the insoluble nitrogen compounds readily decompose into substances which plants can utilise.   N. H. J. M.

Relation of Active Potash to Pot Experiments. GEORGE S. FRAPS (*J. Ind. Eng. Chem.*, 1912, 4, 525—526).—An account of pot experiments with representative Texas soils, from which the conclusions are drawn that (1) the percentage of crops deficient in potash decrease with the increase of active potash in the soil ; (2) the percentage of crops injured by potash increase with the active potash in the soil ; (3) the effect of fertiliser potash on the weight of the crop decreases as the active potash content of the soil increases ; (4) the percentage of potash in the crop increases as the active potash in the soil increases ; (5) the total potash removed by the crop from

the soil increases as the active potash content of the soil increases. The term "active potash" is applied to that which is soluble in $N/5$-nitric acid.   F. M. G. M.

Effect of Sugar on the Fertility of Soils. THEODOR PFEIFFER and EDWIN BLANCK (*Landw. Versuchs-Stat.*, 1912, **78**, 375—388).— The results of plot experiments in which oats, beet, and oats were grown successively both without and with sugar and phosphoric acid, and with both sugar and phosphoric acid, showed that the application of sugar was slightly injurious the first year, and resulted in a slight increase the second year. In the third year there was no appreciable difference due to sugar. No evidence of increased fixation of nitrogen was obtained.   N. H. J. M.

Calcium Cyanamide. C. J. MILO (*Chem. Zentr.*, 1912, ii, 1054—1055 ; from *Med. Proefstat. Java-Suikerind.*, 1912, 427—527). —When calcium cyanamide is used as a manure, the lime is readily taken up and held by the soil, but the nitrogen is not held so well as in the case of ammonium sulphate. In spite of this no nitrogen is lost if the cyanamide is applied in the dry season and the soil is not heavily watered immediately afterwards, and none is lost by volatilisation if the manure is properly applied. The nitrogen is utilised mainly by bacterial agency, but is also absorbed in other ways. Comparison of calcium cyanamide with ammonium sulphate as a manure has not yet given definite results. Dicyanodiamide is not poisonous to sugar-cane, and although calcium cyanamide shows some toxic effects, it appears to be rapidly converted into harmless cyanamide in the soil.

                                                    T. A. H.

Behaviour of Calcium Cyanamide when Stored, and under the Influence of Soil and Colloids. G. HENSCHEL (*Bied. Zentr.*, 1913, **42**, 33—34; from *Cent. Bakt. Par.*, 1912, ii, **34**, 279).—Dry sterilised soil or colloids decompose cyanamide more quickly than when not sterilised. Under sterilised conditions, urea and dicyanodiamide are formed, but no ammonia. Experiments with different soils showed almost complete agreement between the intensity of the decomposition when sterilised and the production of ammonia when not sterilised ; an exception, however, occurred in the case of a sandy soil containing much humus, which showed a strong colloid, but feeble bacterial action.

When cyanamide is stored, a good deal of urea may be produced under some conditions ; different preparations show, however, considerable differences, both in this and other respects. No loss of nitrogen was ever observed, the lower percentages of nitrogen after storing being due to absorption of water and carbon dioxide.   N. H. J. M.

Organic Chemistry.

Some Reactions of Sodamide in the Presence of Liquid Ammonia. Formation of Ethylene Hydrocarbons. E. CHABLAY (*Compt. rend.*, 1913, 156. 327—330).—By the addition of alkyl iodides or chlorides to sodamide in liquid ammonia, primary amines are not the only products as has been supposed (compare Lebeau, A., 1905, i, 401, 512), but at the same time, except in the case of the methyl haloids, the corresponding olefine is formed in varying amounts. Starting from the ethyl haloids, the yield of olefine increases on passing up the series, and is always greater when using the chlorides than if the iodides are employed; thus *iso*butyl iodide gives a yield of 62·4% of *iso*butylene, whilst the chloride gives a yield of 83 6%. In this reaction sodamide resembles alcoholic potassium hydroxide in its behaviour (compare Meunier and Desparmet, A., 1907, i, 186).

W. G.

The Adsorption of Acetylene by Palladium Black. CARL PAAL and CHRISTIAN HOHENEGGER (*Ber.*, 1913, 46, 128—132).—In the previous investigation on the same subject (A., 1910, i, 807), the palladium black was suspended in aqueous solutions of various substances. The authors have now investigated the adsorption of acetylene, using either suspensions of palladium black in pure water, or else dry palladium black. The experiments in which 60% alcohol was used in place of pure water were also repeated.

In all cases the adsorption of the acetylene takes places slowly, and the results given do not point to any fixed ratio between the weight of palladium and the amount of gas adsorbed. It is probable that the acetylene is not completely adsorbed as such, but undergoes partial polymerisation.

When the dry palladium black is not completely free from oxygen, formation of feeble sparks occurs immediately it is brought into contact with the acetylene. T. S. P.

Acetylene or Acetylidene Compounds. The "Oxidation Rearrangement." HEINRICH BILTZ (*Ber.*, 1913, 46, 143—149).—Nef and his school assign to the halogen substitution products of acetylene an acetylidene formula, as, for example, $CI_2{:}O$, di-iodoacetylidene. No definite proof of this constitution has been afforded, and the facts observed are more in favour of the acetylene structure, $CI{:}CI$. Di-iodoacetylene is very readily formed from acetylene by the action of hypoiodites and iodine, the process involving simple substitution of iodine for hydrogen.

The reasons for the representation of dibromoacetylene as $CBr{:}CBr$ are discussed. E. F. A.

Sodium Silver Thiosulphate and Acetylene–Silver Acetylide. KSHITIBHUSHAN BHADURI (*Zeitsch. anorg. Chem,.* 1913, 79, 355—356).—Sodium thiosulphate is added to an ammoniacal solution

of silver nitrate, and acetylene is passed through the clear solution. The yellow precipitate is collected, washed with water and alcohol, and dried in air. It is stable in dry air, but is decomposed by water, yielding a brick-red product. The final products of decomposition are silver sulphide and sodium sulphate.

The yellow compound is soluble in ammonia, and is re-precipitated by acids, again dissolving in an excess to form unstable solutions, which evolve sulphur dioxide and acetylene. Analysis leads to the formulæ $2Na_2S_2O_3,7Ag_2S_2O_3,18Ag_2C_2,32C_2H_2$ for the yellow compound, and $4Ag_2S_2O_3,7Na_2S_2O_3,86Ag_2C_2,13C_2H_2$ for the red compound.

C. H. D.

The Production of Chlorine Substitution Products of Methane from Natural Gas. CHARLES BASKERVILLE and H. S. RIEDERER (*J. Ind. Eng. Chem.*, 1913, **5**, 5—8).—The authors have investigated the conditions necessary for the chlorination of the methane present in natural gas, especially those which would lead to the formation of carbon tetrachloride, from which chloroform could be obtained by reduction. The apparatus used was so designed that the gases could be constantly circulated through it, the circuit always containing a heater for heating the gases, and a condenser for condensing out the products formed. In the first trials the circuit also contained an arc, either between carbon or iron terminals, but this was omitted later, as it was found that chlorination was not effected by the combustion taking place in the arc. It was ultimately found that the primarily important condition for the chlorination is a source of light rich in the rays of the visible blue spectrum, that is, the spectrum from the bluish-green through the visible violet. The ultraviolet part of the spectrum plays little part in the reaction. Apparently the necessary source of light may be obtained by an arc, between iron electrodes, in the circuit, and in some experiments a 20—25% yield of a mixture of carbon tetrachloride and chloroform was obtained.

T. S. P.

Primary Dinitro-, Nitro-nitrite and Dialdoxime Compounds of the Aliphatic Series. II. Derivatives of the Heptane Series and Synthesis of Pimelaldehyde. JULIUS VON BRAUN and E. DANZIGER (*Ber.*, 1913, **46**, 103—110).—As has already been shown (von Braun and Sobecki, A., 1911, i, 830), the action of silver nitrite on aliphatic compounds of the type $I \cdot [CH_2]_n \cdot I$ gives a mixture of dinitro, nitro-nitrite, and dinitrite derivatives, the first two of these being reducible to dialdoximes and amino-alcohols respectively. These changes have already been performed with n equal to 4, 5 and 10, and are now extended to the heptamethylene chain.

$a\eta$-Di-iodoheptane was prepared from $a\epsilon$-dibromopentane by conversion of the latter into an organo-magnesium compound, causing this to react with monochloromethyl ether (compare Dionneau, A., 1906, i, 134) and hydrolysing the product with hydriodic acid. It was also obtained by the stages : dibromopentane, diaminopentane, dichloroheptane, and diphenoxyheptane, the last of which again is converted into di-iodoheptane by hydriodic acid. In the conversion of dichloro-

heptane into diphenoxyheptane by sodium ethoxide, a small quantity of α-phenoxy-ζ-methylene-*n*-hexane, b. p. 145°/12 mm., was obtained as by-product.

αη-Di-iodoheptane reacts vigorously with silver nitrite, producing a mixture which can be separated at 10 mm. into three fractions, b. p 108—140° (mainly *heptamethylene nitrite*, $NO_2 \cdot [CH_2]_7 \cdot NO_2$), 140—160° (mainly *η-nitroheptyl nitrite*), and 160—205°, the last on refractionating yielding pale yellow *αη-dinitroheptane*, b. p. 198—200°/10 mm. The second fraction when reduced with tin and hydrochloric acid yields *η-hydroxyheptylamine*, a strong base, b. p. 150—152°/10 mm. ; *benzoyl*, *nitrobenzoyl*, and *picrate* derivatives are oily ; *platinichloride*, solid, m. p. 157°.

αη-Dinitroheptane when treated with sodium ethoxide in alcoholic solution gives an immediate precipitation of the white *sodium* salt, the aqueous solution of which can be used for the preparation of the salts of the heavier metals, for example, the *copper* (green), *barium* and *calcium* salts ; with bromine, it forms an oily *bromide* (compare von Braun and Sobecki, *loc. cit.*), and with a diazobenzene solution there is obtained yellowish-red *αη-bisphenylazo-αη-dinitroheptane*,

$$N_2Ph \cdot CH(NO_2) \cdot [CH_2]_5 \cdot CH(NO_2) \cdot N_2Ph,$$
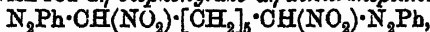
m. p. 139°.

The reduction of a solution of the sodium salt of dinitroheptane by gradual addition to a solution of stannous chloride in hydrochloric acid gives *pimelaldoxime*, $OH \cdot N{:}CH \cdot [CH_2]_5 \cdot CH{:}N \cdot OH$, a pale yellow, crystalline powder, m. p. 150—151°, from which, on boiling with dilute sulphuric acid, pimelaldehyde is not obtained, as it partly polymerises to a viscous oil, and partly becomes dehydrated to tetrahydrobenzaldehyde, semicarbazone, m. p. 211—212° (Wallach, A., 1906, i, 563). *Pimelaldehyde*, a pungent, colourless oil of b. p. 110—112°/13 mm., D_4^{20} 0·9895, is obtainable by the action of nitrous fumes on a suspension of the dioxime in cooled water until no more nitrous oxide is liberated ; it readily reduces Fehling's solution, and an ammoniacal silver solution, and gives a *semicarbazone*, m. p. 183° ; the *phenylhydrazone* and p-*nitrophenylhydrazone* are oily, whilst the *diphenylmethanedimethyldihydrazone*, $CH_2{<}^{C_6H_4 \cdot NMe \cdot N{:}CH}_{C_6H_4 \cdot NMe \cdot N{:}CH}{>}[CH_2]_5$ (structure not proved), is a yellow solid, m. p. 96—97°. The aldehyde resembles adipaldehyde in showing much less tendency to polymerise than do the other dialdehydes of this series.

A preliminary investigation has shown that glutaraldoxime when heated with mineral acids gives pyridine, probably by reason of the condensation of glutaraldehyde and hydroxylamine which are first formed. D. F. T.

Synthesis of an Unsaturated Hydrocarbon. CORNELIS J. ENKLAAR (*Chem. Weekblad*, 1913, **10**, 60—63).—A note on the preparation of unsaturated alcohols by the interaction of unsaturated aldehydes and unsaturated haloids in presence of zinc and ether, and the conversion of such alcohols into unsaturated hydrocarbons by heating with potassium hydrogen sulphate. On treatment with zinc filings or shavings and ether, crotonaldehyde and allyl iodide give a

good yield of $ac\text{-}heptadiene\text{-}\delta\text{-}ol$, $CHMe:CH\cdot CH(OH)\cdot CH_2\cdot CH:CH_2$. Its properties are still uninvestigated, but heating with potassium hydrogen sulphate converts it into a liquid. Repeated fractionation, finally over sodium, at 758 mm. gives three fractions, b. p. $105—110°$, $110—112°$, and $112°$. On cooling to $-76°$, these three fractions solidify. The first has m. p. $-35°$ to $-32°$, the second $-23°$ to $-21°$, and the third $-15°$ to $-14.5°$. One of these substances is believed to be an $a\gamma\epsilon\,heptatriene$, and their constitutions are to be determined. It is anticipated that the method will prove of general application.

A. J. W.

History of Distillation and of Alcohol. EDMUND O. VON LIPPMANN (*Zeitsch. angew. Chem.*, 1913, **26**, 46—47).—Polemical against Schelenz (this vol., i, 2).   T. S P.

Action of Magnesium on a Mixture of Ethyl isoValerate and Allyl Bromide. G. MUSKALENKO (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1862—1865).—Decomposition by means of water of the product of the reaction of magnesium, ethyl isovalerate, and allyl bromide yields $diallylisobutylcarbinol$, $CHMe_2\cdot CH_2\cdot C(OH)(CH_2\cdot CH:CH_2)_2$, which forms a colourless, mobile liquid, b. p. $92°/37$ mm., $D_4^{23}\ 0.8616$, $n_D^{23}\ 1.45682$, and exhibits the normal molecular weight in freezing benzene or boiling ether.   T. H. P.

Adipiopinacone. LOUIS MICHIELS (*Bull. Soc. chim. Belg.*, 1913, **27**, 25—26).—$Adipopinacone$, $OH\cdot CMe_2\cdot[CH_2]_4\cdot CMe_2\cdot OH$, m. p. $88—89°$, is obtained in the form of its $hydrate$, containing $2H_2O$, by the action of magnesium methyl bromide on ethyl adipate. The hydrate is obtained in large, white crystals, m. p. $56.5°$, which effloresce in air, and completely lose their water of hydration when left in a vacuum desiccator. By the action of warm dilute sulphuric acid, the pinacone is readily converted into $tetramethyl$-$hexamethylene$ $oxide$, $O{<}_{CMe_2\cdot CH_2\cdot CH_2}^{CMe_2\cdot CH_2\cdot CH_2}$, a liquid with an ethereal odour, b. p. $156—157°/756$ mm.   W. G.

Action of Magnesium on a Mixture of Allyl Bromide and Ethyl Levulinate. E. SCHTSCHERICA (*J. Russ. Phys Chem. Soc.*, 1912, **44**, 1853—1858).—The interaction of magnesium, allyl bromide (1 mol.), and ethyl lævulate (1 mol.), and subsequent decomposition of the product with water, should yield the ester,

$$C_3H_5\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot CO_2Et,$$
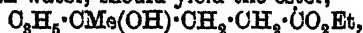
but this reaction could not be realised. No matter whether 1 mol. or 3 mols. of allyl bromide were employed, the resultant compound was always the γ-$glycol$, $C_3H_5\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot C(C_3H_5)_2\cdot OH$, which is a faintly yellow, syrupy, slightly mobile liquid with a characteristic odour, b. p. $157—159°/10$ mm., $D_4^{25}\ 0.9545$, $n_D^{25}\ 1.48712$. When boiled with 20% sulphuric acid solution, the glycol is converted into the corresponding $oxide$, ${}_{CH_2\cdot C(C_3H_5)_2}^{CH_2\cdot CMe(C_3H_5)}{>}O$, which is an almost colour-

less liquid with a peculiar pleasant odour, b. p. 104·5 –105·5°/10 mm., D_4^{25} 0·8905, n_D^{25} 1·46915, and has the normal molecular weight in boiling ether. T. H. P.

Synthesis of Lecithin. Adolf Grün (*Ber.*, 1913, 46, 125—127). —Polemical. A reply, to Langheld (this vol., i, 155; compare Grün and Kade, this vol., i, 158). E. F. A.

Thionium Dibromides of Sulphides. Vladimir V. Tschelincev (*J. Russ. Phys. Chem. Soc.*, 1902, 44, 1885—1894).—The action of bromine on ethyl sulphide in carbon tetrachloride solution yields the thionium dibromide, SEt_2Br_2, which forms yellow crystals and resembles oxonium compounds in its general characters, and also as regards the nature of the solvents in which it dissolves readily or with difficulty. With acetic acid, it forms solid solutions, but in freezing benzene it exhibit, the molecular weight, 199—211, the theoretical value being 250.

By excess of water, the dibromide is rapidly decolorised with develop· ment of a considerable quantity of heat and the formation of a white emulsion. Concentrated ammonia solution decomposes the thionium dibromide much less energetically than the corresponding oxonium compound, heat being developed and an oily layer of the sulphide formed at the surface of the liquid. Sodium hydrogen sulphite solution effects the decomposition rather more rapidly, and concentrated potassium hydroxide solution much more rapidly, than does water. Moist silver oxide converts these dibromides into the corresponding oxides, for example, $SMe_2:O$, which are appreciably more stable than the analogous oxonium compounds.

The heat of formation of the diethyl dibromide from the alkyl sulphide and bromine is 14·15 Cal. per gram-mol., that of the diamyl dibromide being 12·91 Cal. Measurement of the amounts of heat evolved when the reaction proceeds in carbon tetrachloride solutions of various concentrations shows that the solvent is virtually without influence in this respect.

As the heats of formation of the oxonium compounds corresponding with the above thionium compounds are 9·13 Cal. for $OEt_2:Br_2$ and 8·72 Cal. for $O(C_5H_{11})_2:Br_2$, it is to be expected that alkyl sulphides would displace the ethers from oxonium compounds. Calorimetric investiga- tions show that when the oxonium compound is prepared in absence of solvent, such displacement does occur, but does not proceed to com- pletion, at any rate within the limits of time available for calorimetric measurements; it appears probable that the bromine finally becomes distributed between the sulphide and the ether. When, however, a carbon tetrachloride solution of ethyl sulphide (1 mol.) is added to a solution of ether (1 mol.) and bromine (1 mol.) in the same solvent, 13·76 Cal. are developed; as this amount is somewhat less than the theoretical quantity, 14·15 Cal., for complete displacement of the ether from the oxonium compound by ethyl sulphide, it may be that here, too, the bromine is distributed between the sulphide and the ether. T. H. P.

Catalytic Acceleration of the Esterification of Organic Acid by means of Glucinum Compounds. OTTO HAUSFR and A. KLOTZ (*Chem. Zeit.*, 1913, **37**, 146).—Experiments on the solubility of glucinum acetate in various organic solvents have led the authors to the discovery that the rate of esterification of organic acids and alcohols can be considerably increased by the addition of glucinum acetate or hydroxide to the boiling mixture. The catalytic action of glucinum compounds is still more pronounced when the mixed vapours of the acid and alcohol are passed over the oxide heated at 310°. The authors claim that better yields are obtained by this process than by that of Sabatier (actually 70% and over), that there is no loss of catalyst, since the glucinum oxide after use can be regenerated by simple ignition, and that tertiary alcohols and acids of high molecular weight can be esterified in this manner. The following new esters have been prepared : tert.-*butyl* n-*octoate*, b. p. 241°; tert.-*amyl* n-*heptoate*, b. p. 137°, and tert.-*amyl* n-octoate, b. p. 229°.   H. W.

Mechanism of the Action of Bromine on Chlorides of Fatty Acids. ARTHUR MICHAEL and ERWIN SCHARF (*Ber.*, 1913, **46**, 135—138).—When butyryl chloride, saturated with hydrogen bromide at 0°, is heated in sealed tubes at 100°, double decomposition takes place with the formation of butyryl bromide and hydrogen chloride. It is probable therefore that the formation of hydrogen chloride by the action of bromine on acyl chlorides is not due to the decomposition of a bromine additive product, formed from the enolic modification of the chloride, but is brought about by the direct action of the chloride with hydrogen bromide produced during the reaction. This is not in agreement with Lapworth's (T., 1904, **85**, 30) interpretation of the change.

Proof is further given that by the action of bromine on butyryl chloride in sunlight some quantity of the β-derivative as well as the a-derivative is formed. Hydrogen chloride and bromide in equal proportions are liberated on opening the tube. When the contents were converted into the ethyl ester, and hydrolysed with barium hydroxide, considerable quantities of crotonic acid derived from the β-ester were obtained.   E. F. A.

Aliphatic Nitro-compounds. XIII. Preparation of a-Nitro-a-methylbutyric Acid. WILHELM STEINKOPF (*Ber.*, 1913, **46**, 98—100). —An unfinished attempt to prepare a tertiary nitrocarboxylic acid containing an asymmetric carbon atom.

[With HARRY GRUNUPP and LEO HUG.]—A mixture of butanoneoxime with anhydrous hydrogen cyanide is kept in a closed flask for four to eight days at the ordinary temperature, and the excess of acid then removed in a vacuum; crystals of a-*hydroxylamino-a-methylbutyronitrile*, OH·NH·CMeEt·CN, m. p. 61·5°, are obtained. When this substance is oxidised by the cautious addition of an acidified solution of potassium permanganate, a blue *oil* (probably a-nitroso-a-methyl-butyronitrile) is first formed, but disappears later with the production of a-*nitro-a-methylbutyronitrile*, NO_2·CMeEt·CN, an almost colourless oil, b. p. 87—88°/17 mm. Attempts to hydrolyse this to the corre-

sponding acid, or to convert it into an imino-ester hydrochloride were unsuccessful.   D. F. T.

Action of Alkali Sulphites on the Ethylenic Acids.
J. BOUGAULT and MOUCHEL-LA-FOSSE (*Compt. rend.*, 1913, **156**, 396—398).—It being known that, on adding benzoylacrylic acid to a solution of normal or sodium hydrogen sulphite, combination instantly takes place, giving the sodium salt of a saturated sulphonic acid (compare Bougault, *Ann. Chim. Phys.*, 1908, [viii], **15**, 299), the authors have compared the activity of different types of ethylenic acids in this reaction. A large number of ethylenic acids combine in this way with sodium hydrogen sulphite, giving acids of the type $CH_2R\cdot CH(SO_3Na)R'$, which are very soluble in water, and, on heating with aqueous sodium hydroxide to 160°, regenerate the original unsaturated acid. The more energetic is the acid and the more electronegative groups it contains, the more rapid is the fixation of the sodium hydrogen sulphite. Acids such as *cyclo*geranic, undecenoic, and oleic acids, and in general those with long, straight chains, do not combine with the sodium hydrogen sulphite even after prolonged heating. The reaction can be employed to estimate the amount of unsaturated acid in a mixture of saturated and unsaturated acids, and also permits of the separation of the saturated acid in a pure state.
                                                              W. G.

The Salts of Rare Earths with Hydroxycarboxylic Acids.
I. The Glycollates of the Rare Earths. GUSTAV JANTSCH and A. GRUNKRAUT (*Zeitsch. anorg. Chem.*, 1913, **79**, 305—321).—The internally complex salts of rare earths with hydroxycarboxylic acids might be expected to differ more widely in solubility than the normal salts, and therefore to be suitable for the purpose of separation. It is found that the glycollates of the cerium group are anhydrous, and crystallise in crusts, whilst those of the yttrium group crystallise in needles with $2H_2O$. The yttrium salt is the least soluble, then follow the lanthanum, cerium, and praseodymium salts, which are almost equal, and then, in order, the neodymium, samarium, and gadolinium salts. The solutions exhibit the normal reactions, but conductivity determinations show that complexes are present.

Lanthanum hydroxide dissolves in a warm solution of glycollic acid, the solution at first remaining clear, but at a definite temperature, depending only on the concentration, the complex salt separates as a precipitate, $La(C_2H_3O_3)_3$. The praseodymium, neodymium, and samarium salts behave in the same manner.

Gadolinium glycollate, $Gd(C_2H_3O_3)_3,2H_2O$, crystallises without first forming an unstable solution, whilst the yttrium salt behaves like those mentioned above.

The fractionation of the earths from xenotime, previously freed from cerium, has been carried out by adding a solution of sodium glycollate to the hot solution of the mixed nitrates. After each addition, in order to overcome the unstable condition, the mixture is stirred vigorously for two hours at 80—90°. It is then filtered, and the filtrate is treated in similar manner. Successive fractions show a

progressive increase in the atomic weight, whilst the spectra show a concentration of neodymium and praseodymium in the last fractions.

C. H. D.

Succinic Semialdehyde [β-Aldehydopropionic Acid]. EDMOND E. BLAISE and E. CARRIÈRE (*Compt. rend.*, 1913, **156**, 239—241).— A reply to Harries (A., 1912, i, 827), in which the authors uphold the views already expressed by Carrière (A., 1912, i, 410) that β-aldehydopropionic acid changes spontaneously into a polymeride which is termolecular, and that the bimolecular compound, m. p. 147°, of Harries (*loc. cit.*) is the compound obtained by the elimination of $1H_2O$ from two molecules of the aldehyde.   W. G.

General Method for the Preparation of the Ammonium Salts of Organic Acids. EDWARD H. KEISER and L. McMASTER (*Amer. Chem. J.*, 1913, **49**, 84—86).—On account of the hydrolytic action of water on the ammonium salts of organic acids, comparatively few of them have hitherto been prepared, and in the case of most dibasic acids only the ammonium hydrogen salts have been obtained. It has now been found that normal salts can be readily prepared by passing dry ammonia into a solution of the organic acid in ether or alcohol, or a mixture of the two. The salts are insoluble, and separate in the form of white precipitates. *Ammonium maleate, fumarate, mesaconate, citraconate, malonate,* and *phthalate* are described.   E G.

Sebacates and Cacodylates of the Rare Earths O. F. WHITTEMORE and CHARLES JAMES (*J. Amer. Chem. Soc*, 1913, **35**, 127—132; *Chem. News*, 1913, **107**, 75—77).—In an earlier paper (A., 1912, ii, 690) it was shown that yttrium can be separated quantitatively from the alkali metals by precipitation with ammonium sebacate. It has now been found that lanthanum and cerium can also be separated from the alkali metals in this way. The following salts are described: *lanthanum sebacate,* $[C_8H_{16}(CO_2)_2]_3La_2,2H_2O$; *praseodymium sebacate,* $[C_8H_{16}(CO_2)_2]_3Pr_2,2H_2O$; *neodymium sebacate,* $[C_8H_{16}(CO_2)_2]_3Nd_2,3H_2O$; *samarium sebacate,* $[C_8H_{16}(CO_2)_2]_3Sa_2,4H_2O$; *yttrium sebacate,* $[C_8H_{16}(CO_2)_2]_3Yr_2,4H_2O$.

On fractionally precipitating a solution containing chiefly the chlorides of yttrium, dysprosium, and holmium with sodium cacodylate, it was found that yttrium tended to accumulate in the early fractions, and holmium and dysprosium in the later fractions. On boiling a mixture of hydroxides, consisting mainly of those of neodymium, samarium, and gadolinium, with cacodylic acid and fractionally crystallising the cacodylates from hot water, neodymium collected in the more soluble fractions, whilst nearly all the terbium and dysprosium remained in the least soluble portions. The following salts have been prepared: *praseodymium cacodylate.* $(AsMe_2O_2)_6Pr_2,16H_2O$; *yttrium cacodylate,* $(AsMe_2O_2)_6Yr_2,18H_2O$; *thulium cacodylate,* $(AsMe_2O_2)_6Tm_2,16H_2O$.

Neodymium and samarium cacodylates have been described previously (A., 1912, i, 233).

The rare earth cacodylates readily form double salts with other salts, such as the chlorides, nitrates, and sulphates. The following are described: *lanthanum chloride cacodylate,*

$$2La(AsMe_2O_2)_3,LaCl_3,18H_2O ;$$
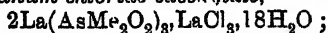
cerium chloride cacodylate, $2Ce(AsMe_2O_2)_3,CeCl_3,18H_2O$, *cerium sulphate cacodylate;* and *neodymium chloride cacodylate,*

$$2Nd(AsMe_2O_2)_3,NdCl_3,18H_2O.$$
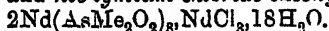
E. G.

The Action of *p*-Bromophenylhydrazine on Glycurono-lactone. GUIDO GOLDSCHMIEDT and ERNST ZERNER (*Ber.*, 1913, **46**, 113—115).—In reply to Jolles (this vol., i, 9), the authors maintain their previous statement (this vol., i, 9), that even with purified *p*-bromophenylhydrazine the test for glycuronic acid is so uncertain as to be of little practical value. D. F. T.

Behaviour of Chloraloxime Towards Water and Alkalis. F. CARLO PALAZZO and V. EGIDI (*Gazzetta*, 1913, **43**, i, 57—69. Compare Palazzo, A., 1912, i, 946; Palazzo and Fazio, 1911, i, 421).—When Meyer's chloraloxime is kept for some days with ten times its weight of water, an acid solution is obtained, from which can be isolated a product having the composition of oximinoacetic acid; it has, however, an indefinite m. p., and is to be regarded as a mixture of two stereoisomerides. It differs from the oximinoacetic acid, m. p. 138°, already known, in yielding a red coloration with ferric chloride. When Meyer's chloraloxime is distilled, several liquid fractions, b. p. 65—85°/20—25 mm., are obtained, and also a portion, b. p. 85°/20 mm., which solidifies and has m. p. 56°. Even if carefully freed from the liquid form, the solid substance yields, when treated with water, a product similar to that given by the original mixture.

By the action of hydroxylamine hydrochloride on bromal hydrate, *bromaloxime* is obtained in acicular crystals, m. p 115°; it has the composition and molecular weight required by the formula

$$CBr_3 \cdot CH:NOH.$$

Oximinoacetic acid forms two *copper* salts, namely, a blue salt,

$$[OH \cdot N:CH \cdot CO_2]_2Cu,2H_2O,$$
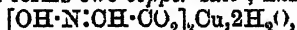
and a dark green salt of the probable composition $\begin{matrix} CH:NO \\ CO_2 \end{matrix}>Cu.$
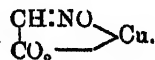
R. V. S.

Inosite-phosphoric Acid. ANTON RICHARD ROSE (*Biochem. Bull.*, 1912, **2**, 21—49).—A useful review with bibliography on the subject. W. D. H.

Syntheses of Alkylgalactosides by means of Emulsin, β-Propylgalactoside and β-Benzyl Galactoside. ÉMILE BOUR-QUELOT, HENRI HÉRISSEY, and MARC BRIDEL (*Compt. rend.*, 1913, **156**, 330—332).—The two galactosides have been prepared from galactose and the corresponding alcohols under the influence of emulsin by the method previously described (A., 1912, i, 946).

β-*Propylgalactoside*, m. p. 105—106° (corr.), $[a]_D$ – 8·86°, crystallises in long, white needles, having a slightly bitter taste. It is not hygroscopic, but is very soluble in alcohol and water, and gives a slight reduction with Fehling's solution.

β-*Benzylgalactoside*, m. p. 100—101°, $[a]_D$ – 25·05°, crystallises in long, white needles, having a disagreeable bitter taste. It is not hygroscopic, and gives but traces of reduction with Fehling's solution. Both of these galactosides are readily hydrolysed by emulsin in aqueous solution.   W. G.

Photochemical Synthesis of Carbohydrates. WALTHER LÓB (*Biochem. Zeitsch.*, 1913, **48**, 257—258).—A reply to Stoklasa, Sebor, and Zdobnický (this vol., i, 18).   S. B. S.

Cellulose. C. PIEST (*Zeitsch. angew. Chem.*, 1913, **26**, 24—30).— The viscosity of a solution of a cellulose nitrate decreases with time and, generally, a deposit settles on the bottom of the vessel containing the solution. Experiments have been made which show that the decrease in the viscosity is not due to the separation of this deposit from the solution.

It has been stated previously that, a diminution in the viscosity of a solution of cellulose nitrate is probably due to the presence of nitrates of oxycelluloses. It is shown now that if a viscous solution of a cellulose nitrate be mixed with a less viscous solution of a nitrate of a highly bleached cotton wool the viscosity of the mixture is considerably less than the calculated value, although if two solutions of the same cellulose nitrate, but of different concentrations (and, therefore, different viscosities), be mixed, the mixture has a viscosity which is very close to the calculated value.

Cellulose, when treated with oxidising agents, is known to yield oxycelluloses, the part soluble in sodium hydroxide solution being termed β-oxycellulose, whilst the insoluble portion is called a-oxycellulose. The results of numerous trials, based on determinations of the "copper value" and viscosity of a standard solution in a cuprammonium solution by Ost's method (compare A., 1911, i, 838), show that a-oxycellulose, when carefully freed from the degradation products grouped under the name β-oxycellulose, is chemically identical with normal cellulose, and differs from it only in that the fibres are much shorter and finer, owing to the attack of the oxidising agent.

It is also shown that the products of the action of acids on cellulose ("hydrocellulose"), or of a hot 30% solution of sodium hydroxide ("alkalised cellulose"; compare Ost and Katayama, A., 1912, i, 680), contain a portion insoluble in sodium hydroxide solutions which is unattacked cellulose.   W. H. G.

Preparation of Higher Aliphatic Chlorinated Amines. JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1913, **46**, 228—231. Compare von Braun and Müller, A., 1907, i, 28).—The bis-imidochlorides of the type $CPhCl:N\cdot[CH_2]_n\cdot N:CPhCl$, obtained by the action of phosphorus pentachloride on the corresponding dibenzoylated diamine, when distilled undergo decomposition mainly into benzonitrile and the

dichloride, but to a slight extent a product $Cl \cdot [CH_2]_n \cdot N:CPhCl$, in which only one of the phenyl radicles has been eliminated, is obtained (compare von Braun and Danziger, A., 1912, i, 597). As the latter class of substance on hydrolysis would give rise to chloroamines, the method might prove valuable if the yield of the second class of product could be increased.

It is now found that at very low pressures the desired decomposition at one end of the chain is greatly favoured.

$\alpha\zeta$-Di-iodohexane reacts with potassium cyanide, giving suberonitrile, $CN \cdot [CH_2]_6 \cdot CN$, b. p. 176—178°/11 mm., which by successive reduction (by sodium and alcohol) and benzoylation is converted into $\alpha\theta$-*dibenzoyl-diamino-octane*, $NHBz \cdot [CH_2]_8 \cdot NHBz$. When the last substance is carefully fused with a bimolecular proportion of phosphorus penta-chloride and the resultant mixture warmed under a pressure of 0·1 mm., there distils into the receiver, which is cooled by liquid air, a mixture of benzonitrile, $\alpha\theta$-dichloro-octane, and θ-*chlorobenzo-octyl-amide*, $COPh \cdot NH \cdot [CH_2]_8 \cdot Cl$, colourless leaflets, m. p. 65°, the last of which is most conveniently purified by means of its *compound* with calcium chloride. θ-Chlorobenzo-octylamide is hydrolysed by hydrochloric acid at 150°, with the formation of θ-*chloro-octylamine*; *hydrochloride*, hygroscopic; *platinichloride*, m. p. 193—194° (decomp.), sparingly soluble. The base on treating its hydrochloride with alkali easily undergoes intramolecular change to a *base*, $C_8H_{17}N$, with an odour resembling pyridine; yellow *platinichloride*, m. p. 197°.

In an analogous manner by the distillation of dibenzoyldiamino-heptane and of dibenzoyldiaminododecane with phosphorus penta-chloride under a pressure of 0·1 mm., η-*chlorobenzoheptylamide*, $Cl \cdot [CH_2]_7 \cdot NHBz$, and μ-*chlorobenzododecylamide*, $Cl \cdot [CH_2]_{12} \cdot NHBz$, m. p. 65°, can be obtained in fair quantity.

The yields were 40%, 30%, and 30% of the theoretical in the heptane, octane, and dodecane series respectively. D. F. T.

Dibromides of Tertiary Amines. VLADIMIR V. TSCHELINCEV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1894—1905).—With a view to the comparison of dibromides obtained from tertiary amines with oxonium and thionium dibromides (compare this vol., i, 245), the author has investigated their solubilities in various solvents, their molecular weights, and their chemical and thermochemical relations.

A general parallelism exists between the solubility of trimethyl-amine dibromide and those of oxonium and thionium dibromides. Also in freezing acetic acid, trimethylamine dibromide has the molecular weight corresponding with the simple formula NMe_3Br_2, and is hence completely analogous to oxonium and thionium compounds in this respect (compare Hantzsch and Graf, A., 1905, i, 575).

Amine dibromides are somewhat more stable than the oxonium compounds towards moisture and are decomposed by ethyl alcohol, yielding hydrogen and ethyl bromides. When treated with excess of bromine, dibromides of amines are converted into new com-pounds, which possess peculiar properties distinguishing them from dibromides and represent a different class of perbromides.

The heat of formation of tripropylamine dibromide from its constituents is 39·72 Cal. per gram-mol., and that of triisoamylamine dibromide, 38·76 Cal. ; the carbon tetrachloride employed as solvent is without influence on the amount of heat developed (see this vol., i, 245).

Thermochemical investigation of the interaction of diethyloxonium dibromide or diethylthionium dibromide and tripropylamine in carbon tetrachloride solution shows that the tertiary amine displaces the ether or ethyl sulphide completely from oxonium or thionium compounds.

Ether has no action on diethyloxonium dibromide, and ethyl sulphide none on diethylsulphonium dibromide, but tertiary amine dibromides react energetically with tertiary amines, forming compounds separating from carbon tetrachloride in a felted mass of slender, pale yellow needles. The following thermochemical data were obtained :

$$2\mathrm{NPr_3Br_2 + NPr_3} = 23\cdot6 \text{ Cal.}$$
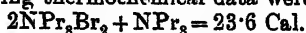
and $2\mathrm{N(C_5H_{11})_3Br_2 + N(C_5H_{11})_3} = 22\cdot9$ Cal. The compounds formed in this way are being investigated further.

Neither the structure suggested by Hantzsch (A, 1905, i, 576) nor that given by Cain (A., 1905, i, 747) for these amine dibromides seems to explain the reactions better than the simple formula.

<div align="right">T. H. P.</div>

Preparation of Oxan and the Properties of Salts of α- and β-Oxan. ALEXANDER P. LIDOV (*J. Amer. Chem. Soc.*, 1913, **35**, 132—134. Compare Abstr., 1912, i, 541).—Oxan is obtained most readily by the action of nitric oxide or nitrous oxide on charcoal at 150—300°. α-Oxan, O·C⫶N, is a stable gas and is not affected by hot platinised asbestos, whilst β-oxan, O·N⫶C, is rapidly decomposed under these conditions. The sodium salt of α-oxan is stable when heated, whilst that of β-oxan decomposes explosively. The silver salt of β-oxan is pale yellow and darkens rapidly on exposure to light; that of α-oxan is white and is less susceptible to the action of light. The iron and calcium salts are also described. The sodium salt of α-oxan gives a white precipitate with manganous chloride or aluminium chloride, whilst that of β-oxan does not yield a precipitate. The salts of α- and β-oxan gradually cease to evolve gas, and this is probably due to polymerisation taking place.

<div align="right">E. G.</div>

Action of Sulphuric Acid on Dicyanodiamide. HJ. LIDHOLM (*Ber.*, 1913, **46**, 156—160).—The interaction of dicyanodiamide with acids to form guanylcarbamide has been studied quantitatively and shown to be a bimolecular reaction. Guanylcarbamide is a sufficiently strong base to be titrated with sulphuric acid and methyl-orange.

Concentrated sulphuric acid acts on dicyanodiamide, liberating carbon dioxide and ammonia and forming guanidine. Guanylcarbamide is decomposed in a similar manner. These observations confirm the structure of dicyanodiamide as guanidinoformonitrile,

$$\mathrm{NH\text{⫶}C(NH_2)\text{·}NH\text{·}CN,}$$
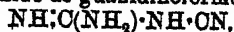
<div align="right">E. F. A.</div>

The Tautomerism of Fulminic Acid. F. CARLO PALAZZO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 713—719. Compare A., 1907, i, 298, 489 ; 1909, i, 776).—The author's work on this subject has led him to conclusions similar to those of Ley and Kissel (A., 1899, ii, 485), according to which fulminic acid is to be regarded as a tautomeric substance related to the pseudo-acids. In the aqueous solution of fulminic acid, there is equilibrium between various saturated and unsaturated desmotropic forms. In the present paper this opinion is developed, and a new argument in its favour is drawn from the behaviour of sodium fulminate with azoimide, for in this reaction the fulminic acid reacts sometimes as carbyloxime and sometimes in the desmotropic form of formonitryl oxide, $HC:N:O$. The products of the reaction are hydroxytetrazole (I), m. p. 145°, and *iso*oxytetrazole (II),

(I.)　　HC——N·OH
　　　　N·N:N

(II.)　　N——CH
　　　　N·NH·N:O
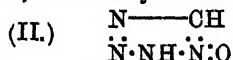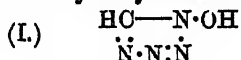
m. p. 156°, and the relative proportions in which these two substances are formed depend on the temperature at which the reaction proceeds.

　　　　　　　　　　　　　　　　　　　　　　　　R. V. S.

Catalysis. XIV. Reversible Addition of Alcohols to Nitriles Catalysed by Ethoxides. I. ELI K. MARSHALL, jun., and SOLOMON F. ACREE [and, in part, C. N. MYERS] (*Amer. Chem. J.*, 1913, **49**, 127—158).—A study has been made of the addition of alcohols to nitriles in presence of ethoxides as catalysts. It has been found that nitriles unite with ethyl alcohol in presence of sodium, potassium or lithium ethoxide, and that in every case the reaction is reversible. The percentage of imino-ester present when equilibrium is attained is the same whether the reaction is started with the nitrile or the imino-ester. The equilibrium point varies widely with the different compounds, the percentages of imino-ester formed with certain nitriles being as follows : butyronitrile, 0·90 ; propionitrile, 1·75 ; acetonitrile, 2·50 ; p-toluonitrile, 6·8 ; benzonitrile, 14·0 ; p-bromobenzonitrile, 27·2 ; m-bromobenzonitrile, 38·0 ; p-nitrobenzonitrile, 62·0 ; m-nitrobenzonitrile, 78·0 ; diisoamylcyanoamide, 98·0. In some cases, the equilibrium point varies considerably with changes in the concentration of the nitrile and the ethoxide, but in other cases shows but little fluctuation. Different ethoxides catalyse the reaction with different velocities, and the equilibrium points also often vary in such cases. The velocity of the reaction varies greatly with the different nitriles, p-nitrobenzonitrile reacting very rapidly, whilst o-toluonitrile scarcely unites with alcohol at all.

Certain experiments are described which show that the velocity of reaction can be expressed as a function of both the ethoxide ions and the non-ionised ethoxide.　　　　　　　　　　　　　　　　E. G.

Nitrile of Fumaric Acid and the Preparation of Methyl Maleate. EDWARD H. KEISER and L. McMASTER (*Amer. Chem. J.*, 1913, **49**, 81—84).—Keiser and Kessler (A., 1911, i, 949) have shown that fumaronitrile can be prepared by heating fumaramide with phosphoric oxide. It has now been found that the nitrile can be

converted into fumaramide by treating it with an alkaline solution of hydrogen peroxide.

Methyl maleate, which has only been obtained previously by the action of methyl iodide on silver maleate, has now been prepared by heating a mixture of maleic acid, methyl alcohol, and sulphuric acid under a reflux condenser. When the ester is left with solution of ammonia for several days, it gradually dissolves, and on evaporation a yellow viscous mass is obtained which is probably maleamide.

<div align="right">E. G.</div>

The Action of Light on Pigments. II. The Composition of Turnbull's Blue. ALEXANDER EIBNER and L. GERSTACKER (*Chem. Zeit.*, 1913, **37**, 137—139, 178—179, 195—197).—As a result of their experiments, the authors come to the conclusion that freshly prepared Turnbull's blue is not identical with Paris blue, but is a derivative of ferricyanic acid. It is not the most labile of the ferricyanides of the heavy metals, those of ferric iron, zinc, cadmium, lead, and copper being less stable. On long-continued washing or heating, a change takes place between the constituents of Turnbull's blue, resulting in the reduction of the ferricyanogen and oxidation of the ferrous radicle. The final result of such treatment is identical with Paris blue, the velocity of change depending on the conditions.

<div align="right">T. S. P.</div>

Spirocyclane, its Synthesis and Behaviour on Catalytic Reduction. NICOLAI D. ZELINSKI (*Ber.*, 1913, **46**, 160—172; *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1873—1884).—The hydrocarbon formed by the action of zinc dust and alcohol on the tetrabromide of pentaerythritol has been regarded by Gustavson (A., 1896, i, 669) as vinyltrimethylene. Reasons are now given for formulating the compound as spirocyclane, $\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}\!>\!C\!<\!\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}$. The only other possible constitution is that of methylene*cyclo*butane.

The hydrocarbon is very readily and completely reduced in contact with nickelised asbestos and hydrogen at about 100°. No condensation product is formed, the gaseous mixture consisting entirely of saturated hydrocarbons. This behaviour eliminates any other constitution than that of the spirocyclane.

[With V. KRAVEC.]—This is confirmed by effecting the synthesis of spirocyclane by closing the two trimethylene rings one after the other.

By the action at 0° of hydrogen bromide on pentaerythritol, the *dibromohydrin*, $C(CH_2Br)_2(CH_2 \cdot OH)_2$, is obtained. This crystallises in well formed needles, m. p. 112°; the *diacetyl* derivative has b. p. 185°/13 mm.

When reduced with zinc dust, the *diacetate* of *dimethylolcyclopropane* is obtained, b. p. 115°/15 mm. The *glycol*,

$$\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}\!>\!C(CH_2 \cdot OH)_2,$$
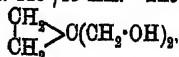
has b. p. 126—127°/16 mm., D_4^{20} 1·0794, $n^{20\cdot5}$ 1·4705. When oxidised with permanganate, it yields *cyclo*propane-1 : 1-dicarboxylic acid.

Phosphorus tribromide converts the glycol into *dibromodimethyl-cyclopropane*, $\begin{matrix} CH_2 \\ CH_2 \end{matrix} > C \cdot (CH_2Br)_2$, b. p. 72—74°/13 mm., D_4^{20} 1·8022, $n = 1·534$. In addition, a tribromide resulting from the opening of the *cyclo*propane ring is formed.

On reduction of the dibromide, spirocyclane is obtained, b. p. 40—41·5°, D_4^{20} 0·7266, $n = 1·4120$, in agreement with earlier values.

[With B. SCHTSCHERBAK.]—When a mixture of spirocyclane and hydrogen is passed over platinum black at 70°, a mixture of ethyl-*cyclo*propane and pentane is formed. Using palladium black in the cold, it is possible to restrict the reduction entirely to one ring and obtain ethyl*cyclo*propane alone. In order to reduce the second ring, nickel must be used as catalyst—a temperature of 200° is necessary before *iso*pentane is obtained. The reduction of spirocyclane thus takes place in two stages and selective catalysts are required. Nickel in the cold reduces it only to ethyl*cyclo*propane. E. F. A.

Preparation of the Three Cymenes (Methyl*iso*propylbenzenes) and Three Menthanes (Methyl*iso*propyl*cyclo*hexanes). PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, **156**, 184—187. Compare Sabatier and Senderens, A., 1901, i, 459).—Starting from the three tolyldimethylcarbinols, $C_6H_4Me \cdot CMe_2 \cdot OH$, the authors have prepared the three corresponding cymenes and menthanes, and examined their physical properties. The three carbinols were prepared either (1) by the action of magnesium methyl iodide on the ethyl o-, m-, and p-toluates, or on the three tolyl methyl ketones, or (2) by the action of acetone on the three magnesium tolyl bromides. The vapours of the three carbinols were completely dehydrated under the influence of thorium oxide at 350°, giving respectively o-, m-, and p-β-allyltoluene, $C_6H_4Me \cdot CMe \colon CH_2$, which by the action of slightly activated nickel at 200—220° yielded the corresponding cymenes. These substances underwent further hydrogenation when passed in the form of vapour over activated nickel at 170—180°, and the corresponding menthanes were obtained, all of which have been previously described. In certain cases the values of the physical constants now obtained differ from those previously given by other authors, namely, o-β-allyltoluene has b. p. 175°, D_0^{16} 0·9181, n_D^{16} 1·521 (compare Tiffeneau, A., 1907, i, 305).

o-Cymene has b. p. 175° (corr.), D_0^{0} 0·8902, n_D^{22} 1·501 (compare Sprinkmeyer, 1901, i, 519).

o-Menthane, b. p. 171° (corr.), D_0^{0} 0·8326, D_0^{21} 0·8135, n_D^{21} 1·447 (compare Kay and Perkin, T., 1905, **87**, 1066).

r-m-Menthane, b. p. 166—167° (corr.), D_0^{24} 0·7968, n_D^{24} 1·440.

d-m-Menthane was obtained by the hydrogenation of natural d-sylvestrene at 200° by activated nickel, and has b. p. 167—168°, D_0^{0} 0·8235, D_0^{23} 0·8116, n_D^{23} 1·446, $[\alpha]_D^{23}$ +1·60° (compare Knoevenagel, A., 1897, i, 610).

The para-isomeride has b. p. 167—168° (corr.), D_0^{0} 0·8134, D_0^{25} 0·8028, n_D^{25} 1·440 (compare Sabatier and Senderens, *loc. cit.*). W. G.

Systems Formed by Chloro- and Nitro-toluenes with Antimony Trihaloids. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1939—1963).—o-, m-, and p-Chlorotoluenes melt at − 36·2°

(Haase, A., 1892, ii, 357, gave $-34°$), $-47·8°$, and $6·2°$ (Haase, *loc. cit.*, gave $7·4°$) respectively.

With antimony trichloride, *o*-chlorotoluene forms the compound, $SbCl_3,C_6H_4MeCl$, crystallising in long plates or needles, m. p. 3°, and the eutectic points and compositions are (1) 37·5° and
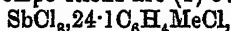
$$SbCl_3,24·1C_6H_4MeCl,$$

and (2) $-0·5°$ and $SbCl_3,1·950C_6H_4MeCl$. *m*-Chlorotoluene gives the compound, $SbCl_3,C_6H_4MeCl$, which is much less stable than that formed by the ortho-derivative and decomposes before melting; the eutectic points are (1) $-14°$, $SbCl_3,2·7C_6H_4MeCl$, and (2) $-49°$, $SbCl_3,24·1C_6H_4MeCl$. *p*-Chlorotoluene and antimony trichloride form no compound, the diagram showing only one eutectic point at $-7·5°$, corresponding with $SbCl_3,2·3C_6H_4MeCl$.

With antimony tribromide, none of the chlorotoluenes form compounds. The eutectic points and the corresponding compositions are for the ortho-compound, $-38·5°$ and $SbBr_3,23·8C_6H_4MeCl$; for the meta-compound, $-50°$ and $SbBr_3,32·3C_6H_4MeCl$, and for the para-compound, 2·5° and $SbBr_3,9·4C_6H_4MeCl$.

o-Nitrotoluene has m. p. $-8·5°$ (Knoevenagel, A., 1907, i, 202, gave $-9·4°$, and Ostromisslensky, A., 1907, i, 120, $-10·56°$) for the more stable α-modification and $-4°$ for the less stable β-form; the solutions in antimony trihaloid always correspond with the α-compound. The meta- and para-isomerides melt at 16° and 52·5° respectively.

o-Nitrotoluene and antimony trichloride give the compound
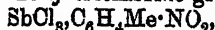
$$SbCl_3,C_6H_4Me·NO_2,$$

crystallising in slender needles, m. p. 34·5°; the eutectic points are $-18·5°$, corresponding with $SbCl_3,7·28C_6H_4Me·NO_2$, and 27·5° with $SbCl_3,0·56C_6H_4Me·NO_2$. *m*-Nitrotoluene and antimony chloride form a compound, which apparently melts at a higher temperature than the corresponding para-compound, but could not be obtained crystalline.

p-Nitrotoluene and antimony chloride form a compound
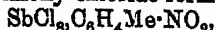
$$SbCl_3,C_6H_4Me·NO_2,$$

which crystallises with difficulty; the eutectic points and compositions are : (1) 7·5° and $SbCl_3,1·55C_6H_4Me·NO_2$, and (2) 3° and

$$SbCl_3,0·76C_6H_4Me·NO_2.$$
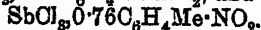
With antimony tribromide, *o*-nitrotoluene forms the compound $SbBr_3,C_6H_4Me·NO_2$, crystallising in needles, m. p. 32° (decomp.), isomorphous with those of the corresponding compound of antimony trichloride. The system exhibits one eutectic point, $-13·5°$, corresponding with $SbBr_3,10·8C_6H_4Me·NO_2$, and one transition point, 31°, corresponding with $SbBr_3,1·3C_6H_4Me·NO_2$. *m*-Nitrotoluene and antimony tribromide form no compound, the system showing only one eutectic point, $-9°$, corresponding with $SbBr_3,2C_6H_4Me·NO_2$. The para-derivative also forms no compound with the tribromide, the diagram consisting of two curves meeting at the eutectic point, 16°, for which the composition is $SbBr_3,1·3C_6H_4Me·NO_2$.

These results are discussed in relation to those obtained with benzene and its other substituted derivatives (*loc. cit.*).   T. H. P.
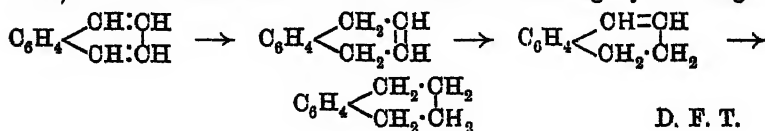
$Δ^1$-**Dihydronaphthalene.** FRITZ STRAUS and LEO LEMMEL (*Ber.*, 1913, **46**, 232—241).—If $Δ^2$-dihydronaphthalene, which was obtained

by Bamberger and Lodter (A., 1888, 292 ; 1896, i, 99) by the action of sodium and ethyl alcohol on naphthalene, is heated with an alcoholic solution of sodium ethoxide, it quantitatively undergoes isomeric change into the hitherto unknown Δ^1-dihydronaphthalene.

Crude Δ^2-dihydronaphthalene was purified by shaking in ethereal solution with an aqueous solution of mercuric acetate ; the crystalline mercury compound, after washing with ether, was dissolved in benzene, when a slight insoluble residue was obtained, apparently of the mercury compound of Δ^1-dihydronaphthalene, due to a trace of this hydrocarbon in the crude starting substance. The pure mercury compound, m. p. 119—120°, obtained on evaporation of the solution, when decomposed with a 30% solution of hydrochloric acid, gave pure Δ^2-dihydronaphthalene, leaflets, m. p. 24 5—25°, b. p. 94·5°/17 mm., which on heating for eight hours at 140—150° with sodium ethoxide in alcoholic solution was isomerised into Δ^1-*dihydronaphthalene*, b. p. 84—85°/12 mm., m. p. −8° to −7°, an unpleasant-smelling liquid which immediately decolorises permanganate ; when shaken with mercuric acetate, it is slowly converted into a white *mercury* derivative, which is insoluble in benzene, and does not melt below 250° ; the *dibromide*, colourless crystals, m. p. 70—71°, is quite distinct from that (m. p. 71·5—72°) of the Δ^2-isomeride, and when boiled with alcoholic potassium hydroxide gives an oily *substance* of characteristic odour, together with a little naphthalene.

When an emulsion of Δ^1-dihydronaphthalene in water is oxidised by the gradual addition of concentrated potassium permanganate solution, *o*-carboxyphenylpropionic acid is obtained, together with a quantity of a pungent *substance* of low m. p. The further reduction of Δ^1-dihydronaphthalene can be accomplished by the addition of its alcoholic solution to finely-divided sodium, the product being tetrahydronaphthalene.

The above method of formation of Δ^1-dihydronaphthalene disposes of the difficulty of reconciling the reduction of naphthalene through Δ^2-dihydronaphthalene to tetrahydronaphthalene with the behaviour of the analogous allylbenzene and propenylbenzene, only the latter of which is reducible by sodium and alcohol to a saturated homologue of benzene (Klages, A., 1903, i, 19, 329 ; 1904, i, 567) ; according to this, Δ^2-dihydronaphthalene should not be directly reducible. The preparation of tetrahydronaphthalene by Bamberger and Kitschelt (A., 1890, 1146) is to be attributed to the reduction occurring by the stages

$$C_6H_4{<}^{CH:CH}_{CH:CH} \rightarrow C_6H_4{<}^{CH_2\cdot CH}_{CH_2\cdot CH} \rightarrow C_6H_4{<}^{CH:CH}_{CH_2\cdot CH_2} \rightarrow$$

$$C_6H_4{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2} \qquad\qquad \text{D. F. T.}$$

Triphenylmethyl. XXII. Ethers or Oxides in the Triphenylmethane Series. Moses Gomberg (*J. Amer. Chem. Soc.*, 1913, **35**, 200—210).—It is well known that diarylcarbinols can be converted into the corresponding ethers or oxides by heating them either alone or in presence of a dehydrating agent. A few oxides of the triaryl-

carbinols have also been reported in the literature, but the results of the present work show that most of the compounds thus designated were not in reality triarylmethyl ethers.

A general method is now described for the preparation of triarylmethyl ethers. These compounds are as stable as the peroxides, are not affected by exposure to the air, or by heating them to temperatures below their m. p.; they are not decomposed by water or dilute alkali hydroxide, even at 100°, but are hydrolysed when boiled with dilute acids, alcohol, acetic acid, or acetyl chloride.

When triphenylmethyl chloride is treated with silver oxide, oxidation takes place with formation of diphenylquinomethane and other products, but the ether is not obtained. If triphenylmethyl chloride is shaken with zinc oxide and ether in sealed tubes, it is reduced quantitatively to triphenylmethane, and this reaction furnishes a simple and rapid method for preparing the hydrocarbon. The oxides of cadmium, lead, nickel, cobalt, and magnesium do not react with triphenylmethyl chloride. When, however, a triarylmethyl chloride dissolved in a dry solvent, such as benzene, ether, carbon disulphide, or chloroform, is heated on the water-bath with mercuric oxide, the corresponding triarylmethyl ether is readily obtained in a good yield.

Triphenylmethyl ether, $CPh_3 \cdot O \cdot CPh_3$, m. p. 235—237° (decomp.), forms white crystals, and is soluble in about 25 parts of benzene at the ordinary temperature, or in 5 parts of boiling benzene; 1 gram dissolves in 11 c.c. of carbon disulphide or in 325 c.c. of ether.

Phenylfluorene ether, $\left(\substack{C_6H_4 \\ C_6H_4} > CPh \right)_2 O$, m. p. 232—233°, forms colourless crystals, and is soluble in about 6·5 parts of benzene or 100 parts of ether; it is readily converted into the peroxide, m. p. 193° (Gomberg and Cone, A., 1906, i, 822). The compound obtained by Kliegl (A., 1905, i, 187) by the action of acetic and sulphuric acids on phenylfluorenol is not identical with the ether now described.

Phenylxanthenol ether, $\left(O < \substack{C_6H_4 \\ C_6H_4} > CPh \right)_2 O$, m. p. 250—252°, forms pale yellowish-pink crystals, and is soluble to the extent of 1 gram in 12 c.c. of cold, or 5 c.c. of hot, benzene, or in 160 c.c. of ether.

p-*Methoxytriphenylmethyl ether*, m. p. 212°, is soluble to the extent of 1 gram in 25 c.c. of cold benzene.

p-*Acetoxytriphenylmethyl chloride*, m. p. 85—86°, obtained by the action of hydrogen chloride on a solution of the carbinol in benzene, forms white crystals; when treated with mercuric oxide, it is converted into p-*acetoxytriphenylmethyl ether*, m. p. 123—124° (decomp.), which crystallises in white needles, and is not identical with the substance to which this constitution was assigned by Bistrzycki and Herbst (A., 1901, i, 702); the latter was probably the carbinol as suggested by Auwers and Schroter (A., 1903, i, 821).

Another method has also been devised for preparing triarylmethyl ethers. When triphenylmethyl carbonate is heated under certain conditions, carbon dioxide is evolved and a nearly quantitative yield of triphenylmethyl ether is produced. The details of this method will be published subsequently. E. G.

Triphenylmethyl Ether. Moses Gomberg (*Ber.*, 1913, **46**, 225—228).—Although *triphenylmethyl ether* is not obtained in the action of silver oxide on triphenylmethyl chloride (compare Schlenk, this vol., i, 34), the application of mercuric oxide gives an almost quantitative yield of this substance (m. p. 235—237°) The reaction with mercuric oxide is a general one for the production of triaryl-methyl ethers. Triphenylmethyl carbonate (m. p. 205—210°) when heated with copper as a catalyst to 140°, also decomposes into triphenylmethyl ether and carbon dioxide.

The opinion is expressed that the behaviour of triphenylmethyl and its analogues is best explained by an equilibrium between the three structures represented by the tervalent carbon, the hexaphenylethane, and Jacobson's (A., 1905, i, 186) formulæ.

D. F. T.

Synthesis of Pyrene. Richard Weitzenbock (*Monatsh.*, 1913, **34**, 193—223).—Two schemes for the synthesis of pyrene have been followed. The first, which should have led to the preparation of

diphenyl-2 : 2'-diacetaldehyde, which might have condensed in a manner analogous to the formation of β-phenylnaphthalene from phenylacetaldehyde (Auwers and Keil, A., 1904, i, 26), was unsuccessful. The tetramethylacetal of the dialdehyde was obtained, but on hydrolysis it gave 4 : 5 : 6 : 7-dibenzo-$\Delta^{1\cdot4\cdot6}$-*cyclo*heptatriene-2-aldehyde (annexed formula), the ready closing of the seven-membered ring recalling the formation of 2-imino-1-cyano-4 : 5 : 6 : 7-di-benzo-$\Delta^{4\cdot6}$-*cyclo*heptadiene from diphenyl-2 : 2'-diacetonitrile (Kenner and Turner, T., 1911, **99**, 2104).
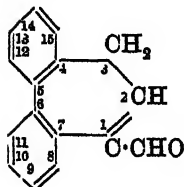
The other scheme was analogous to the preparation of 2 : 8-di-hydroxychrysene from βγ-diphenyl-aδ-dihydromuconic acid (Beschke, A., 1911, i, 874), and consisted in the condensation of diphenyl-2 : 2'-diacetic acid to dihydroxypyrene which could be reduced by means of zinc dust or hydriodic acid and red phosphorus.

Scheme A.—It was first attempted to prepare diphenyl-2 : 2'-diacrylic acid by the distillation of *methyl o-iodocinnamate*, white needles, m. p. 40°, b. p. 300—310°, with copper, but the decomposition proceeded to the formation of phenanthrene. The ethyl ester could not be obtained pure, and gave still worse results. The acid was obtained, however, by Perkin's synthesis on 2 : 2'-dialdehydodiphenyl (compare Mayer, A., 1911, i, 870), being accompanied by the lactone of diphenyl-2-carbinol-2'-carboxylic acid (Kenner and Turner, *loc. cit.*), and was converted into the *diamide*, $C_{18}H_{16}O_2N_2$, white needles, by means of thionyl chloride and ammonia.

A better way to arrive at diphenyl-2 : 2'-diacetaldehyde was sought in the application of Weerman's method (A., 1907, i, 132) to the *amide* of o-*iodocinnamic acid*. This was obtained by the action of thionyl chloride and ammonia on the acid, in light brown, quadratic leaflets, m. p. 204—205°, the crude chloride having m. p. 63—64°. When treated with sodium hypochlorite in methyl alcohol, *methyl*

o-*iodostyrylcarbamate*, $C_6H_4I\cdot CH{:}CH\cdot NH\cdot CO_2Me$, was obtained in colourless leaflets, m. p. 128—130°, which on hydrolysis gave o-*iodophenylacetaldehyde*, C_8H_7OI, in pleasant smelling, white needles, m. p. 35—36°. When heated with copper, extensive decomposition took place, which was also the case with the *phenylbenzylhydrazone*,

$$C_{21}H_{19}N_2I,$$

stout, colourless needles, m. p. 104—105°. However, the *dimethylacetal*, $C_{10}H_{13}O_2I$, which was obtained by Fischer and Hoffa's method (A., 1898, i, 659) as a colourless, mobile oil, b. p. 144°/19 mm., gave a good yield of diphenyl-2 : 2'-diacetaldehyde,

$$C_{12}H_6\cdot[CH_2\cdot CH(OMe)_2]_2,$$

in the form of a viscid, yellow oil, b. p. 210—211°/13 mm. On hydrolysis, an unsaturated aldehyde was obtained, in white, pleasant smelling needles, m. p. 108—109°, which gave phenanthraquinone on oxidation with chromic acid, and is, therefore, to be regarded as 4 : 5 : 6 : 7-*dibenzo*-Δ-$^{1:4:6}$-*cycloheptatriene* 1-*aldehyde*, rather than as phenanthryl-4-acetaldehyde. It gives a stable *dibromide*, $C_{10}H_{12}OBr_2$, in colourless needles, m. p. 133° (decomp.).

Scheme B.—Diphenyl-2 : 2'-diacetonitrile was hydrolysed by means of concentrated hydrochloric acid at 130—140° (compare Kenner and Turner, *loc. cit.*), and the acid was dehydrated with zinc chloride or, better, converted into the chloride with thionyl chloride and then condensed with aluminium chloride. The impure, reddish hydroxy-product gave pyrene when distilled with zinc dust or heated with hydriodic acid and red phosphorus at 200°. An attempt to convert dibromoditolyl into the nitrile by Mann's method for phenylacetonitrile (A., 1881, 1034) resulted in the formation of Kenner and Turner's 2-imino-1-cyano-4 : 5 : 6 : 7-dibenzo-$\Delta^{4:6}$-*cyclo*heptadiene.　　J. C. W.

Quaternary Salts of Alkylideneamines and a General Method of Converting Primary into Secondary Amines. HERMAN DECKER and PAUL BECKER (*Annalen*, 1913, **395**, 362—377). —The formation of a quaternary ammonium salt by the addition of an alkyl iodide to an alkylideneamine is practicable, but the product is often contaminated by other substances formed by (i) the dissociation of the salt into its generators, (ii) heterosperisis (Decker and Fellenberg, A., 1909, i, 116), (iii) intramolecular change, ring formation, or polymerisation of the salt.

Quaternary alkylideneammonium iodides are decomposed by water or alcohol in the sense of the equation :

$$CHR''{:}NRR'I + H_2O = R''\cdot CHO + NHRR' + HI,$$
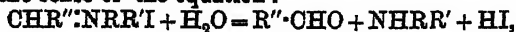
whereby a very satisfactory method is secured of converting primary into secondary amines without any possibility of the formation of the tertiary amines or the quaternary salt. The yield of the secondary amine is usually more than 75%, being less, however, in the case of primary aromatic amines containing the amino-group in the nucleus.

β-Phenylethylamine reacts with benzaldehyde and with vanillin on the water-bath to form β-*phenylethylbenzylideneamine*,

$$CH_2Ph\cdot CH_2\cdot N{:}CHPh,$$
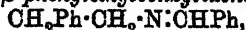
m. p. 33—34°, colourless prisms, and β-*phenylethylvanillylidenea* in

m. p. 108—109°, leaflets, respectively. The former and methyl iodide at 100° yield an additive compound which is decomposed by boiling 95% alcohol into benzaldehyde and *β-phenylethylmethylamine h driodide*, $CH_2Ph \cdot CH_2 \cdot NHMe,HI$, m. p. 113—115°. The base, which is also produced by heating β-phenylethylglycine above its m. p., forms a *hydrochloride*, m. p. 156—157° (decomp.), *platinichloride*, m. p. 225—226° (decomp.), and *picrate*, m. p. 141—143°. β-Phenylethylethylamine, prepared in a similar manner, forms a *hydriodide*, m. p. 166—168°. Methyl-*p*-toluidine, prepared in a similar manner from benzylidene *p*-toluidine or heptylidene-*p*-toluidine, forms a *hydriodide*, m. p. 134—137°, pale yellow leaflets, and a *picrate*, m. p. 130—132° (decomp.), which is very sparingly soluble in benzene. Ethylaniline, methylaniline, and methyl*iso*butylamine have also been prepared by this method. C. S.

The Nitro-derivatives of *o*-Cresyl Oxide [*o*-Tolyl Ether] and *o*-Cresylene Oxide [Di-*o*-tolylene Oxide]. ALPHONSE MAILHE (*Compt. rend.*, 1913, **156**, 241—243. Compare this vol., i, 173).—On nitrating *o*-tolyl ether in acetic acid solution, a viscous liquid is obtained which, by distillation under reduced pressure, yields *5-nitro-o-tolyl ether*, $C_6H_4Me \cdot O \cdot C_6H_3Me \cdot NO_2$, yellow needles, m. p. 125°; this on reduction with iron and acetic acid gives the corresponding *amine*, m. p. 98°. If the nitration is effected in cold fuming nitric acid, by gradual addition of the ether to the acid, 5 : 5'-*dinitro-o-tolyl ether*, $O(C_6H_3Me \cdot NO_2)_2$, is obtained as a white powder, m. p. 270°, which on prolonged nitration with fuming nitric acid, containing a little sulphuric acid, is converted into 3 : 5 : 3' : 5'-*tetranitro-o-tolyl ether*,

$$O[C_6H_2Me \cdot (NO_2)]_2,$$

m. p. 115°.

Di-*o*-tolylene oxide nitrates very readily in acetic acid solution on warming, giving *nitrodi-o-tolylene oxide* $O{<}^{C_6H_3Me}_{C_6H_2Me \cdot NO_3}$, m. p. 108—109°, giving by reduction the corresponding *amine*, m. p. 92°, which gives a red coloration in alcoholic solution with calcium chloride.

By warming di-*o*-tolylene oxide with fuming nitric acid, a *dinitro*-derivative is obtained, crystallising in yellow needles, m. p. 170°. By warming this compound with fuming nitric acid, *tetranitrodi-o-tolylene oxide*, $O{<}^{C_6H Me(NO_2)_2}_{C_6HMe(NO_2)_2}$, is obtained as a white powder, m. p. 210°.

W. G.

The Action of Aldehydes on Phenols. HERMANN WICHELHAUS (*Ber.*, 1913, **46**, 110—112).—A continuation of research as to the origin of the dyes in certain woods (compare A., 1910, i, 868).

Formaldehyde has been detected in certain trees (Curtius and Franzen, A., 1912, ii, 978 ; Kleinstück, A., 1912, ii, 1202), and the author has, therefore, examined the action on phenols of trithioformaldehyde, which possesses the advantage of a lower volatility. In the presence of zinc chloride, condensation occurs with β-naphthol, resor-

cinol, α- and β-anthrols, and dihydroxynaphthalene, producing deeply coloured fusions which are difficult to purify. It is probable that one molecule, CH_2S, condenses with two of the phenol.

If the aldehyde is first combined with sodium sulphite (D.R.-P. 87335), the condensation follows another course, involving two molecules of aldehyde and two of the phenol; the products are colloidal substances often yielding fluorescent solutions, and possess dyeing power.

β-Naphthol after conversion into the acid, $OH \cdot C_{10}H_6 \cdot CH_2 \cdot SO_3H$, gives a condensation product which in solution possesses a green fluorescence, dyes wool a rose colour, and gives brightly coloured lakes with aluminium, manganese, and zinc salts. The product from β-naphtholsulphonic acid dyes silk greyish red.

2 : 7-Dihydroxynaphthalene when converted into 2 : 7-dihydroxy-naphthylmethanesulphonic acid, and heated slowly with zinc chloride solution in a vacuum, undergoes condensation below 100°, giving a blue *substance*, $C_{32}H_{16}O_6$; this dyes silk, and also can be converted into *nitro*-derivatives which also possess dyeing properties.

<div align="right">D F. T.</div>

The Silver Equivalent of Quinol. M. A. GORDON (*J. Physical Chem.*, 1913, **17**, 47—82).—The number of molecules of silver salt reduced per molecule of quinol varies with the conditions up to at least 10·5. In presence of acid no reduction occurs. In alkaline solution the amount of silver liberated from precipitated silver bromide depends on the efficiency of stirring, the time, temperature, and concentration of the alkali, but not on the incident light. At 20° in presence of excess of sodium hydroxide, the action appears to proceed in two stages, namely, up to about 6 equivalents of silver in a few hours, and then to about 8 in eighteen days. At 100° at least 9 equivalents are liberated in six hours.

The silver equivalent of *p*-benzoquinone is about two less than that of quinol. The liberation of 6 equivalents of silver by quinol corresponds with the formation of dihydroxy-*p*-benzoquinone, thus:

$$C_6H_4(OK)_2 + 6AgBr + 6KOH = C_6H_2(OK)_2O_2 + 6Ag + 6KBr + 4H_2O.$$

p-Benzoquinone and monohydroxy-*p*-benzoquinone may be intermediate products as suggested by Luther and Leubner (*Brit. J. Photo.*, 1912, **59**, 632—747), although the presence of neither monohydroxy- nor dihydroxy-benzoquinone has been demonstrated. *p*-Benzoquinone is undoubtedly an intermediate product, and by the action of the alkaline solution is transformed into quinol plus a peroxidised product which may be hydrogen peroxide (Mees and Sheppard) or hydroxybenzoquinone (Luther and Leubner). The Mees and Sheppard theory demands an infinite liberation of silver by a small amount of quinol in presence of sodium sulphite, and is inadmissible. The Luther and Leubner theory restricts the silver equivalent of quinol to 6, and therefore does not express the whole truth.

In strongly alkaline solution an excess of sodium sulphite increases the silver equivalent of quinol by 2 (from 6 to 8) for short runs, and by 1 (from 8 to 9) for long runs. The effect on the equivalent of benzoquinone is about half as great. When sulphite is added after the reduction by quinol has started, its effect is restricted. Hence

sulphite probably intervenes in the first and second stages of the oxidation of quinol equally. Some of the sulphite is oxidised, presumably to dithionate, although sodium sulphite alone is without action on silver bromide.

Ammoniacal silver nitrate, silver sulphite dissolved in sodium sulphite, and silver oxide in presence of sodium hydroxide give quinol equivalents of 7, 8, and 10·5 respectively for five minute runs.

Pyrogallol with and without sodium sulphite has a silver equivalent of a little over 3 when tested with silver bromide in a one hour run. Catechol under like conditions has an equivalent of 4·5, increasing to 5·5 in presence of sulphite. R. J. C.

o-Nitrophenyl Selenocyanate and *o*-Aminophenylselenol. HUGO BAUER (*Ber.*, 1913, **46**, 92—98).—When a solution of potassium selenocyanate is added gradually to a diazotised solution of *o*-nitroaniline in which the excess of free mineral acid has been neutralised by the addition of sodium acetate, nitrogen is liberated and a quantitative yield of *o-nitrophenyl selenocyanate*, yellow needles, m. p. 142°, is obtained. This action appears to be a general one, and was also successful with *p*-nitroaniline (p-*nitrophenyl selenocyanate*, pale yellow leaflets, m. p. 135°), sulphanilic acid, *p*-aminobenzoic acid, and arsanilic acid. On moistening with alcohol and then adding sodium hydroxide solution, *o*- and *p*-nitrophenyl selenocyanates undergo hydrolysis, forming coloured solutions (violet and red respectively) of the *sodium* salts of *o*- and p-*nitrophenylselenols*; the free phenylselenols could not be isolated, but the addition of a solution of lead acetate precipitated the *lead* salts, both of an orange colour.

The coloured alkaline solution of *o*-nitrophenylselenol soon loses its colour, undergoing oxidation even in a hydrogen atmosphere to *di-o-nitrophenyl diselenide*, yellow needles, m. p. 209°, which precipitates. The alkaline solution of *o*-nitrophenylselenol can also be obtained by the interaction of *o*-chloronitrobenzene and sodium hydroselenide in dilute solution in cold alcohol, and the diselenide can then be again obtained, the oxidation being aided if necessary by the addition of hydrogen peroxide. The former method is, however, the more satisfactory.

If the alkaline solution of *o*-nitrophenylselenol is treated near its b. p. with sodium hyposulphite a clear yellow or colourless solution of the *sodium* salt of *o-aminophenylselenol* is obtained, which on careful oxidation with hydrogen peroxide gives a precipitate of *di-o-aminophenyl diselenide*, orange needles, m. p. 81°. When a solution of this in hot alcohol is treated with hydrochloric acid and the resultant suspension of the *hydrochloride* reduced by zinc dust, the addition of sodium acetate precipitates the stable *zinc* salt of *o*-aminophenylselenol; the action of lead acetate on a suspension of this gives the orange *lead* salt. The reduction of the diselenide can also be effected by alkali and dextrose (compare Clasz., A., 1912, i, 851).

The action of benzoyl chloride on the zinc salt of *o*-aminophenylselenol in the presence of ethyl acetate produces 1-*phenylbenzoselenazole*, $C_6H_4{<}{\overset{N}{\underset{Se}{}}}{>}CPh$, colourless needles, m. p. 116—117° which could not

be obtained by the action of selenium on benzanilide (compare Hofmann, A., 1880, 386; 1887, 839). With picryl chloride the zinc salt undergoes condensation with the formation of 3:5-*dinitropheno-selenazine*, $C_6H_4 {<}{>}_{Se}^{NH} C_6H_2(NO_2)_2$ (compare Kehrmann, A., 1900, i, 61).   D. F. T.

Some Compounds of Cholesterol giving Liquid Crystals.
PAUL GAUBERT (*Compt. rend.*, 1913, **156**, 149—151. Compare A., 1907, ii, 932; 1908, i, 882; 1909, i, 920).—On heating cholesterol with the different tartaric acids for one minute a homogeneous isotropic liquid substance is obtained, which on cooling yields elongated rhombic crystals, possessing very great plasticity. The direction of the greatest refraction coincides with the long diagonal. At temperatures near to the point of fusion, the crystalline particles of the crystals arrange themselves so that the optical axis is perpendicular to the glass slide, and there are produced extensive, irregular films exhibiting all the characteristics of a uniaxial, optically positive substance. The hardness of the crystals rapidly increases up to that of gypsum as they become solid. Similar results are obtained by using malic and lactic acids instead of the tartaric acids. Maleic and malonic acids, but not fumaric acid, yield optically positive liquid crystals almost instantly on warming with cholesterol, but they are only stable within narrow temperature limits. The same applies to the compound obtained with succinimide and cholesterol. In order to obtain liquid crystals with cholesterol and succinic, cinnamic, or anisic acids, it is necessary to keep the mixture molten at 160° for one hour, when characteristic optically negative crystals are produced.
                                                                                W. G.

Action of Magnesium on a Mixture of Allyl Bromide and Benzoin. V. JAKUBOVITSCH (*J. Russ. Phys. Chem. Soc*, 1912, **44**, 1858—1861).—*Diphenylallylethylene glycol* [δε-diphenyl-Δª-pentene-δε-*diol*], $C_3H_5 \cdot CPh(OH) \cdot CHPh \cdot OH$, prepared by decomposing with water the product of the action of magnesium on allyl bromide and benzoin, forms small, colourless crystals, m. p. 89°, has the normal molecular weight in boiling benzene, and decolorises bromine. When boiled with 20% sulphuric acid, it is converted into the corresponding double *ether*, $\begin{matrix} CHPh\text{---}O\text{---}CHPh \\ CPh(C_3H_5) \cdot O \cdot CPh \cdot C_3H_5 \end{matrix}$, which crystallises in small, colourless needles, m. p. 125—126°.   T. H. P.

Influence of Constitution on the Rotatory Power of Optically Active Substances. V. **Esters of *d*-Carvoxime.** HANS RUPE and GEORG WOLFSLEBEN (*Annalen*, 1913, **395**, 136—148).—The following substances have been prepared generally by the interaction of *d*-carvoxime, pyridine (2 mols.), and the acyl chloride in benzene. Only the acetyl compound can be purified by distillation under diminished pressure; the others must be crystallised from absolute or dilute alcohol. Acetylcarvoxime has m. p. 63—64°, b. p. 158—161°/17 mm., and and $[a]_D^{20}$ +43·02°. *Crotonylcarvoxime*, $C_{10}H_{14}{:}NO \cdot CO \cdot CH{:}CHMe$, oil,

$[a]_D^{20}$ +33·46°; *diphenylacetylcarvoxime*, m. p. 65—66°, $[a]_D^{29}$ +17·63°; *cinnamoylcarvoxime*, m. p. 79°, $[a]_D^{20}$ +15·44°; *β-phenylpropionylcarvoxime*, oil, $[a]_D^{20}$ +26·23°; *a-phenylcinnamoylcarvoxime*,

$$C_{10}H_{14}{:}N{\cdot}O{\cdot}CO{\cdot}CPh{:}CHPh,$$

m. p. 139—140°, $[a]_D^{20}$ +37·06°; *aβ-diphenylpropionylcarvoxime*, m. p. 119—120°, $[a]_D^{20}$ +12·52°; *β-phenylcinnamoylcarvoxime*, m. p. 74—75°, $[a]_D^{20}$ +26·37°; *di-β-phenylpropionylcarvoxime*, m. p. 89—90°, $[a]_D^{20}$ +20·09°; *a-methylcinnamoylcarvoxime*, m. p. 68—69°, $[a]_D^{20}$ +16·33°; *β-phenyl-a-methylpropionylcarvoxime*, oil, $[a]_D^{20}$ +23·85°; *β-methylcinnamoylcarvoxime*, m. p. 78°, $[a]_D^{20}$ +22·45°; *β-phenyl-β-methylpropionylcarvoxime*, oil, $[a]_D^{20}$ +22·76°.

Excluding the *a*- and the *β*-phenylcinnamoyl- and diphenylpropionyl-carvoximes, the rotation of the saturated or the alkyl derivatives is distinctly greater than that of the corresponding unsaturated or phenyl derivatives. A parallelism cannot be traced between the carvoxime esters and the menthyl esters of the acids.

The entrance of a phenyl group into acetic acid or phenylacetic acid or the replacement of methyl by phenyl in acetic acid or crotonic acid diminishes the rotatory power of the carvoxime; the entrance of phenyl into the *a*- or the *β*-position in cinnamic acid increases the rotatory power. Just the converse behaviour is observed with the menthyl esters of the acids. The author is of opinion that the work so far recorded proves the necessity of dealing with substances containing one, or at most two, asymmetric carbon atoms in connexion with the problem of the relation between constitution and rotatory power. C. S.

The Determination of the Configuration of the Stereoisomeric Cinnamic Acids. CARL LIEBERMANN (*Ber.*, 1913, 46, 214—216).—A reply to Stoermer and Heymann (A., 1912, i, 974), indicating that theirs is not the first experimental proof of the steric configuration of *allo*cinnamic acid. D. F. T.

Fixation of the Alkali Hydrogen Sulphites by the Salts and Esters of the Acetylenic Acids. ED. LASAUSSE (*Compt. rend.*, 1913, 156, 147—149).—Under given conditions the salts or esters of the acetylenic acids of the type $R{\cdot}C{:}C{\cdot}CO_2H$ will unite with one or two molecules of an alkali hydrogen sulphite, giving an alkali salt of a monosulphonic acid, containing an ethylenic linking, or of a saturated disulphonic acid.
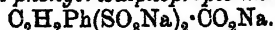
On heating phenylpropiolic acid (1 mol.) with normal sodium sulphite (1·5 mol.) in aqueous solution, in a sealed tube for eight hours at 100°, crystals of *disodium-β-sulphocinnamate*,

$$SO_3Na{\cdot}CPh{:}CH{\cdot}CO_2Na,$$

are obtained, which rapidly decolorise potassium permanganate in the cold. When heated in sealed tubes at 130° with concentrated hydrochloric acid it is decomposed, giving carbon dioxide, sulphur dioxide, and acetophenone. On fusion with sodium hydroxide at 200—220°, it yields sodium benzoate, sodium acetate, and sodium sulphite. The corresponding *potassium* salt has been prepared, starting with potassium sulphite. Methyl phenylpropiolate and sodium hydrogen sulphite under similar conditions yield *sodium methyl sulphocinnamate*,
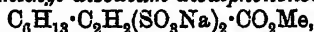
$$SO_3Na{\cdot}CPh{:}CH{\cdot}CO_2Me.$$
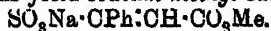
If the heating is carried on for forty hours under reflux instead of in sealed tubes, three compounds are obtained, namely, *methyl disodium disulphophenylpropionate*, $C_2H_3Ph(SO_3Na)_2 \cdot CO_2Me$, disodium sulphocinnamate, and *sodium phenyldisulphopropionate*,
$$C_2H_2Ph(SO_3Na)_2 \cdot CO_2Na.$$
These three substances can be separated by their varying solubility in alcohol. The *barium* salt corresponding with the last compound has been prepared.

By similar methods the author has prepared *methyl disodium disulpho-octoate*, $C_5H_{11} \cdot C_2H_2(SO_3Na)_2 \cdot CO_2Me$, which is saponified by cold aqueous sodium hydroxide, giving the corresponding *trisodium* salt, which when heated with hydrochloric acid in sealed tubes at 120° yields the *acid*, $C_5H_{11} \cdot C_2H_2(SO_3Na)_2 \cdot CO_2H$.

He also prepared *methyl disodium disulphononoate*,
$$C_6H_{13} \cdot C_2H_2(SO_3Na)_2 \cdot CO_2Me,$$
the *trisodium* derivative, and the *acid*, $C_6H_{13} \cdot C_2H_2(SO_3Na)_2 \cdot CO_2H$.
<div align="right">W. G.</div>

Synthesis of β-m-Tolyl-α-methylhydracrylic Acid. A. GUBAREV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1865—1867).—*Ethyl β-m-tolyl-α-methylhydracrylate*, $C_6H_4Me \cdot CH(OH) \cdot CHMe \cdot CO_2Et$, obtained by decomposing with water the product of the action of zinc on a mixture of ethyl α-bromopropionate and *o*-tolualdehyde, is a colourless, viscous liquid, with a pleasant odour, b. p. 171—172°/15—16 mm. The *acid* forms crystals, m. p. about 90°, but was not obtained pure. The *potassium* ($+ H_2O$), *silver*, *zinc*, *copper*, and *lead* salts were prepared, and the first two analysed.
<div align="right">T. H. P.</div>

Influence of Constitution on the Rotatory Power of Optically Active Substances. IV. HANS RUPE (*Annalen*, 1912, **395**, 87—135).—[With EDUARD LENZINGER.]—The following menthyl esters have been prepared by heating menthol and the substituted ethyl acetoacetate; acetoacetate, m. p. 36°, b. p. 154°/10 mm.; *methylacetoacetate*, $CH_3 \cdot CO \cdot CHMe \cdot CO_2 \cdot C_{10}H_{19}$, b. p. 148—149°/8 mm., $[a]_D^{20}$ $-63.59°$ in benzene, n_a 1·45436, n_D 1·45733, n_β 1·46317, n_γ 1·46797, D_4^{20} 0·9697, violet coloration with alcoholic ferric chloride; ethylacetoacetate, b. p. 155°/8 mm., $[a]_D^{20}$ $-60.26°$ in benzene, violet coloration with ferric chloride. The following menthyl esters are prepared by heating menthyl sodioacetoacetate and the requisite alkyl haloid in ethyl alcohol: *propylacetoacetate*, b. p. 162°/8 mm., $[a]_D^{20}$ $-57.27°$ in benzene, reddish-violet coloration with alcoholic ferric chloride; sec.-*octylacetoacetate*, b. p. 139°/0·1 mm., $[a]_D^{20}$ $-47.82°$ in benzene, brownish-red coloration with ferric chloride. *Menthyl phenylacetoacetate*, prepared from menthol and ethyl phenylacetoacetate at 140°, has m. p. 69°, b. p. 131—133°/0·1 mm., and develops a violet coloration with alcoholic ferric chloride. A freshly prepared solution of the ester in benzene is dextrorotatory, $[a]_D^{20}$ $+19.07°$, but rapidly becomes lævorotatory, and has $[a]_D^{20}$ $-67.55°$ constant after ten days. In another experiment, $[a]_D^{20}$ was initially $+28.70°$, and finally constant at $-67.16°$ after sixty-seven days. In alcohol, $[a]_D^{20}$ is initially $-28.27°$, and becomes constant at $-67.15°$ after forty-seven hours.

Menthyl benzylacetoacetate, prepared from menthol and ethyl benzyl-acetoacetate at 155°, has m. p. 68°, and $[a]_D^{20}$ – 106·97°, and pioduces with alcoholic ferric chloride a yellow coloration ch inging to greyish-yellow. By treatment with benzyl bromide and alcoholic sodium ethoxide at 0°, it yields *menthyl dibenzylacetoacetate*, m. p. 70°, $[a]_D^{20}$ – 25·28°.

Menthyl sodioacetoacetate and the requisite haloid in alcohol yield the following menthyl esters : *β-phenylethylacetoacetate*,

CH₂Ph·CH₂·CHAc·CO₂·C₁₀H₁₉,
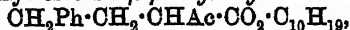
b. p. 143°/0·1 mm., $[a]_D^{20}$ – 51·64° in benzene and – 53·79° in alcohol, violet coloration with ferric chloride ; *γ-phenylpropylacetoacetate*, b. p. 157°/0·1 mm., $[a]_D^{20}$ – 45·44° in benzene and – 48·99° in alcohol ; *allyl-acetoacetate*, b. p. 169—171°/13 mm., $[a]_D^{20}$ – 58·27° in benzene ; *cinnamylacetoacetate*, CHPh:CH·CH₂·CHAc·CO₂·C₁₀H₁₉, $[a]_D^{20}$ – 41·31° in benzene.

Menthyl benzoylacetate, CH₂Bz·CO₂·C₁₀H₁₉, prepared from ethyl benzoylacetate and menthol at 120°, has m. p. 41°, $[a]_D^{20}$ n benzene initially – 55·36° and finally – 63·97° after fifty hours, $[a]_D^{20}$ in alcohol initially – 56·41° and finally – 56·89° after six hours, is slightly soluble in alkalis, develops a deep red coloration with alcoholic ferric chloride, and forms a *semicarbazone*, m. p. 163°, which produces a dark green coloration with ferric chloride.

The following menthyl esters are obtained by treating menthyl sodiobenzoylacetate with the requisite alkyl haloid in alcohol ; *a-benzoylpropionate*, CHMeBz·CO₂·C₁₀H₁₉, m. p. 68°, $[a]_D^{20}$ – 57·73° in alcohol ; *a-benzoylbutyrate*, b. p. 208°/10 mm., $[a]_D^{20}$ – 55·86° in alcohol and – 54·27° in benzene ; *a-benzoylvalerate*, decomp. 180°/0 mm., $[a]_D^{20}$ – 52·35° in alcohol, violet-red coloration with alcoholic ferric chloride.

Ethyl benzoylphenylacetate and menthol at 160—165° yield *menthyl benzoylphenylacetate*, m. p. 116°, $[a]_D^{20}$ + 20·14° in benzene and – 12·12° initially and – 62·60° after eighty-nine hours in alcohol.
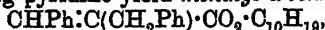
The following menthyl esters are obtained from menthyl sodio-benzoylacetate and the requisite haloid in alcohol : *a-benzoyl-β-phenyl-propionate*, m. p. 117°, $[a]_D^{20}$ – 60·83° in benzene ; *a-benzoyl-γ-phenyl-butyrate*, m. p. 77°, $[a]_D^{20}$ – 56·70° in benzene ; *a-benzoyl-δ-phenylvalerate*, $[a]_D^{20}$ – 43·97° ; *a-benzoyl-Δγ-pentenoate*, m. p. 53°, $[a]_D^{20}$ – 51·40° in benzene, violet-red coloration with ferric chloride in alcohol ; *a-benzoyl-δ-phenyl-Δγ-pentenoate*, m. p. 82—83°, $[a]_D^{20}$ – 48·10°.

By esterifying a-benzoyl-δ-phenyl-Δγ-pentenoic acid with menthol and repeatedly extracting the product with gasolin, it can be resolved in the sparingly soluble l-*menthyl* l-*a-benzoyl-δ-phenyl-Δγ-pentenoate*, m. p. 102—103°, $[a]_D^{20}$ – 86·66° in benzene, colourless needles, and the more soluble l-*menthyl* d-*a-benzoyl-δ-phenyl-Δγ-pentenoate*, m. p. 77°, $[a]_D^{20}$ – 25·95° in benzene ; the esters do not develop a coloration with alcoholic ferric chloride.

Menthyl benzoylacetate and benzaldehyde and a little piperidine, cooled in a freezing mixture, yield *menthyl a-benzoylcinnamate*, CHPh:CBz·CO₂·C₁₀H₁₉, m. p. 65°, $[a]_D^{20}$ – 77·43° in benzene white leaflets.

[With PAUL HÄUSSLER.]—a-Benzylcinnamoyl chloride and mentho

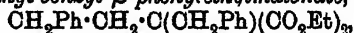in benzene containing pyridine yield *menthyl α-benzylcinnamate*,
$$CHPh:C(CH_2Ph)\cdot CO_2\cdot C_{10}H_{19},$$
m. p. 64—65°, $[a]_D^{20}$ – 144·86° in benzene, and *α-benzylcinnamic anhydride*, $O[CO\cdot C(CH_2Ph):CHPh]_2$, m. p. 108—109°. The latter, which is stable to boiling aqueous sodium carbonate and is only slowly esterified by boiling alcohol and sulphuric acid, is also obtained directly from the acid chloride and pyridine.

Menthyl β-phenyl-α-benzylpropionate, m. p. 42—43°, $[a]_D^{20}$ – 24·41° in benzene, is prepared from the acid chloride, menthol, and pyridine in benzene.

[With GEORG WOLFSLEBEN.]—The reaction between potassium γ-phenylbutyrate and an excess of benzaldehyde and of acetic anhydride at 106° for forty-eight hours, and subsequently on the water-bath for 290 hours, leads to the formation of *γ-phenyl-α-benzylidenebutyric acid*, $CH_2Ph\cdot CH_2\cdot C(:CHPh)\cdot CO_2H$, m. p. 124—125°. Its *menthyl* ester, prepared from the acid chloride, menthol, and pyridine in benzene, is a yellow oil, $[a]_D^{20}$ – 23·00°.

Ethyl sodiomalonate and β-phenylethyl bromide in boiling alcohol yield *ethyl β-phenylethylmalonate*, $CH_2Ph\cdot CH_2\cdot CH(CO_2Et)_2$, b. p. 179°/10 mm., which reacts with alcoholic sodium ethoxide and benzyl bromide to form *ethyl benzyl-β-phenylethylmalonate*,
$$CH_2Ph\cdot CH_2\cdot C(CH_2Ph)(CO_2Et)_2,$$
b. p. 230°/10 mm. By hydrolysis with methyl alcoholic potassium hydroxide, the latter yields *benzyl-β-phenylethylmalonic acid*, m. p. 153° (decomp.), which is converted at 160° into *γ-phenyl-α-benzylbutyric acid*, $CH_2Ph\cdot CH_2\cdot CH(CH_2Ph)\cdot CO_2H$, m. p. 59—61°, b. p. 230°/8 mm. The acid chloride of the latter yields the *menthyl* ester, m. p. 102°, $[a]_D^{20}$ – 36·69°, by treatment with menthol and pyridine in benzene, and is converted by distillation under 15 mm. partly into 2-*β-phenylethyl-hydrindone*, $C_6H_4\!\!<^{CO}_{CH_2}\!\!>CH\cdot CH_2\cdot CH_2Ph$, m. p. 56—57° (*semicarbazone*, m. p. 227—228° [decomp.]). γ-Phenylpropyl bromide and potassium cyanide yield *γ-phenylbutyronitrile*, b. p. 132—133°/11 mm. The acid is converted by phosphorus trichloride in benzene into the *chloride*, b. p. 119°/9 mm., from which *menthyl γ-phenylbutyrate*, b. p. 205°/10 mm., $[a]_D^{20}$ – 57·00°, is obtained by means of menthol and pyridine in benzene.

The variations with time of the rotations of the preceding menthyl esters of β-ketonic acids in alcohol and in benzene have been measured in order to gain some idea of the magnitude and the velocity of the keto-enolic transformation. The acetoacetate and benzoylacetate rapidly acquire a constant rotation in a alcohol, but only after many hours or even days in benzene; the methylacetoacetate, benzoylpropionate, and benzoylphenylpropionate have constant rotations in benzene as well as in alcohol.

An unexpected fact of great importance has been found in the resolution by crystallisation of the menthyl esters of β-ketonic acids of enantiomorphous configuration. Such esters, the phenyleto-acetate, benzylacetoacetate, benzoylphenylacetate, and benzoylphenyl-pentenoate, all of which, it will be observed, contain a phenyl group, must have the ketonic structure. The case of the menthyl phenyl-

acetoacetate is interesting. Only l-menthyl d-phenylacetoacetate has been isolated, and it is dextrorotatory. As it changes to the enol in benzene, the activity due to the acidic portion disappears, the activity finally being due to the l-menthyl group only ; the time required for the attainment of a constant lævorotation varies in different experi· ments (probably owing to the action of a catalyst in the glass), in one case being ten days and in another sixty-five days The converse is observed with l-menthyl d-benzoylphenylacetate, which has a constant dextrorotation in benzene, but is lævorotatory in alcohol, reaching a maximum after four days.

Menthyl benzyl-, dibenzyl-, and benzylidene-acetoacetates, and the methyl-, phenyl-, benzyl-, s-phenylethyl-, cinnamyl-, and benzylidene-derivatives of menthyl benzoylacetate do not develop a coloration with alcoholic ferric chloride. In some cases the enolisation must be repressed by the ferric chloride, because menthyl benzoylphenylacetate, for example, which does not give a coloration with alcoholic ferric chloride, shows in alcohol a lævorotation which increases with time.

The author's results show that valuable conclusions regarding structure can be drawn from the molecular rotations, provided strictly homologous esters are being compared ; comparisons are not justifiable when an alkyl group is replaced by a phenyl group. C. S.

α-Hydroxy-γ-phenylcrotonic Acid. An Example of an Ether of a Ketone Hydrate. J. BOUGAULT (*Compt. rend.*, 1913, **156**, 236—239. Compare A., 1912, i, 770, and Fittig, A., 1898, i, 196).—By the controlled action of dilute sodium hydroxide on α-hydroxy-γ-phenylcrotonamide, and subsequent neutralisation with acid, an *acid amide* is obtained having the constitution

$$CH_2Ph \cdot CH_2 \cdot C(OH) \cdot CO_2H$$
$$\begin{array}{c} >O \\ CH_2Ph \cdot CH_2 \cdot C(OH) \cdot CO \cdot NH_2 \end{array},$$
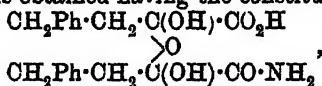
which on heating loses two molecules of water, giving another *acid amide*, $C_{20}H_{19}O_4N$. The first compound is readily decomposed by alkalis or alkali carbonates quantitatively into ammonia and benzyl-pyruvic acid, but unlike the acid anhydrides is not hydrated by boiling with water or dilute acetic acid. W. G.

Esters of Aromatic Keto-acids. GRETE EGERER and HANS MEYER (*Monatsh.*, 1913, **34**, 69—93. Compare A., 1908, i, 26).— The pseudo- and normal esters of some benzoylated benzoic acids are described. In most cases the ψ-methyl esters, for which the sensitive colour reaction with concentrated sulphuric acid is characteristic, are produced by the action of thionyl chloride, but Goldschmiedt and Lipschitz had already shown (A., 1905, i, 132) that the n-ester resulted in the case of naphthoylbenzoic acid, whilst ψ-ethyl esters were hitherto unknown. It is now demonstrated that the ψ-ester is the primary product in all cases, but that under the influence of alcohol and mineral acids it may undergo further changes which result in the n-ester. To prevent this rearrangement, for example, in the case of the naphthoyl-benzoate, the mixture of the acid chloride and the alcohol is immediately poured into sodium carbonate solution. On the other hand, any ψ-ester may be converted into its isomeride by the action of

a mineral acid or thionyl chloride and an alcohol. In this way a
ψ-methyl ester may be transformed into a *n* ethyl ester, which might
be supposed to be due to the effect of mass action on the already
rearranged *n*-methyl ester. Since, however, prolonged heating with
methyl alcohol is necessary to convert ethyl *n*-benzoylbenzoate into the
n-methyl ester, whereas the ψ-ethyl ester gives the *n*-methyl ester in a
short time, the conclusion is drawn that the transformation of the
ψ-form into the *n*-form is not due to any instability of the chloride or of
the ester, but to the addition of alcohol to the lactone system under the
catalytic influence of hydrogen ions and the subsequent elimination of
alcohol from the methane carbon atom according to the scheme :
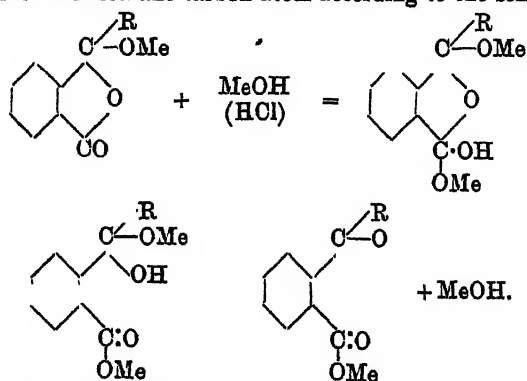
It thus becomes evident why the action of ammonia on the iso-
merides always results in the same amide, namely, that of the ketone
acid (compare Meyer, A., 1905, i, 133).

Some of the acids employed were derived from the chlorophthalic
acid which Auerbach obtained by the action of hypochlorites on
phthalic acid. Since this may be condensed with benzene and trans-
formed into β-chloroanthraquinone, it is to be regarded as 4-chloro-
phthalic acid.

Whereas methyl ψ-benzoylbenzoate may be prepared without pre-
caution, by the action of thionyl chloride and methyl alcohol, the
formation of the ψ-*ethyl* ester only succeeds when the mixture of the
chloride with excess of cold absolute alcohol is at once poured into cold
sodium carbonate solution. It crystallises in triangular tablets, m. p.
51—53°, and dissolves with lemon-yellow colour in concentrated
sulphuric acid. The *n*-ethyl ester (rhombic, $a:b:c = 1.9725 : 1 : 1.267$)
may be prepared by leaving the chloride with alcohol, by the usual
means or by boiling the ψ-methyl ester for a few minutes or the
n-methyl ester for a few hours with alcohol and thionyl chloride or
sulphuric acid. Conversely, methyl alcohol and thionyl chloride
transform the ψ ethyl ester into the *n*-methyl ester in a short time,
whereas the *n*-ethyl ester must be heated for fifty hours. In the same
way, methyl ψ-toluoylbenzoate and methyl ψ-methoxybenzoylbenzoate
(Meyer and Turnau, A., 1909, i, 710; m. p. 83° and not 63°) may be
converted into the *n*-esters.

The preparation of 4-chlorophthalic anhydride by Auerbach's

method has been improved; the compound has b. p. 291—295°, and when crystallised from dry ether has m. p. 94°, but after contact with moist ether the m. p. rises to that of the acid. When condensed with benzene in presence of an excess of aluminium chloride, it yields *benzoyl-4-chlorobenzoic acid*, m. p. 180·5°, which gives β-chloroanthraquinone (Graebe and Rée, T., 1886, 531) in concentrated sulphuric acid. The *acid chloride*, $COPh \cdot C_6H_3Cl \cdot COCl$, long needles, m. p. 114—117°, also readily yields the quinone on heating. The ψ *methyl* ester forms colourless needles, m. p. 68·5—69·5°, and the n-*ester* forms monoclinic crystals ($a : b : c = 1·8252 : 1 : 0·6878$; $β = 76°59'$), m. p. 102—104°.

The acid obtained by the condensation of 4-chlorophthalic anhydride with chlorobenzene dissolves in sulphuric acid with the formation of 2 : 6-dichloroanthraquinone, and is, therefore, 2-p-*chlorobenzoyl-4-chlorobenzoic acid*, which confirms the position of the halogen in the above benzoyl-4-chlorobenzoic acid. The acid has m. p. 195·5°, gives a well-defined *acid chloride*, m. p. 115—120°, from which, however, the ψ-ester could not be obtained crystalline. The n-*methyl* ester, from the transformation of the crude isomeride or by direct esterification, melts at 98°.

Methyl ψ-p-*chlorobenzoylbenzoate*, m. p. 101—102·5°; the n-*ester*, m. p. 109—110°, monoclinic crystals ($a : b : c = 0·92461 : 1 : ?$; $β = 73°40'$), and the n-*ethyl* ester, m. p. 88°, have also been prepared.

Phthalic anhydride condenses with p-dichlorobenzene when boiled with an excess of aluminium chloride in nitrobenzene; the 2-om-*dichlorobenzoylbenzoic acid*, radiating needles, m. p. 168°, yields 1 : 4-dichloroanthraquinone (Ullmann and Billig, A., 1911, i, 490). Similarly, 4-chlorophthalic anhydride and p-dichlorobenzene give 2-om-*dichlorobenzoyl-4-chlorobenzoic acid*, m. p. 157—160°, which condenses to form 1 : 4 : 7-trichloroanthraquinone and yields a ψ-*methyl* ester, m. p. 115—120°.

The constitution of the isomeric esters (A., 1908, i, 26) receives support from the molecular refractions, for methyl n-benzoylbenzoate, $[M.R.]_D = 67·98$, being a benzophenone derivative, shows exaltation (compare Auwers and Eisenlohr, A., 1911, ii, 782), whereas the ψ-ester gives the theoretical value for a hydroxylactone, $[M.R.]_D = 65·40$.

<div style="text-align: right">J. C. W.</div>

Isomeric Esters of Trichlorobenzoylbenzoic Acids. STEPHAN JAROSCHY (*Monatsh.*, 1913, **34**, 1—6. Compare preceding abstract). —The product of the condensation of 1 : 4-dichlorophthalic anhydride with chlorobenzene, 2-p-*chlorobenzoyl-3 : 6-dichlorobenzoic acid*,

$$C_{14}H_7O_3Cl_3,$$
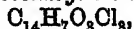
crystallises in colourless leaflets, m. p. 157°, and yields 1 : 4 : 7-trichloroanthraquinone in concentrated sulphuric acid. The ψ-*methyl* ester, colourless crystals, m. p. 153—154°, and the ψ-*ethyl* ester, a white, crystalline powder, m. p. 150—151°, may be obtained by immediately adding the mixture of alcohol and acid chloride to sodium carbonate solution, and may be transformed into the n-esters by heating with thionyl chloride and the corresponding alcohol for some hours. The normal esters may also be obtained by the usual methods, give no

coloration in sulphuric acid, and melt at 90° and 105—106° respectively.   J. C. W.

Preparation of Amides and Acylation of the Amino-group.

HERMAN DECKER (*Annalen*, 1913, **395**, 282—299).—Hofmann's classical method of preparing amides and substituted amides by heating the ammonium salts of carboxylic acids or their salts with primary and secondary amines, which has fallen into disuse owing to its supposed disadvantages, is shown to be a simple and convenient method of preparation provided the optimum temperature (the temperature at which water is eliminated, it may be slowly, from the salt, whilst the dissociation of the latter is still hardly appreciable) is obtained, and is retained to the end of the reaction. A whole series of amides and substituted amides have thus been prepared by simply heating the acid and the amine at the optimum temperature. The reaction, which is analogous to the formation of an ester from an acid and an alcohol, is accelerated, as in the case of esterification, by catalysts.

[With WALTER KROPP, HEINRICH HOYER, CLEMENS ZOELLNER, and PAUL BECKER.]—Formophenylethylamide is obtained free from β-phenylethylamine formate, and in 96% yield by heating β-phenylethylamine and anhydrous formic acid in slight excess at 170—180° for four hours. In a similar manner, phenylacetyl-β-phenylethylamine (95% yield) is obtained from phenylacetic acid and the amine at 180°, and acetyl-β-phenylethylamine from acetic acid and the amine.

Piperonylacetamide, $CH_2O_2:C_6H_3·CH_2·CH_2·CO·NH_2$, m. p. 122—123°, colourless leaflets, can be prepared from the acid chloride and 25% aqueous ammonia, from *ethyl piperonylacetate*, b. p. 303°, and aqueous ammonia at 160—180° (bad yield), or from 3 : 4-methylenedioxy-phenylpropionyl chloride and 25% aqueous ammonia, is readily obtained by heating piperonylacetic acid for two hours at 200—220° in a current of dry ammonia. It is readily converted by the sodium hypochlorite method into homopiperonylamine (hydrochloride, m. p. 207—208°; picrate, m. p. 174—176°; *carbonate*, m. p. about 110°; *platinichloride*, m. p. about 225° [decomp.]).

Formohomopiperonylamide, $CH_2O_2:C_6H_3·CH_2·CH_2·NH·CHO$, m. p. 61—62°, is obtained almost quantitatively from the amine and anhydrous formic acid at 180—200°. *Phenylacetohomopiperonylamide*, $CH_2O_2:C_6H_3·CH_2·CH_2·NH·CO·CH_2Ph$, m. p. 96°, is obtained from the amine and phenylacetic acid at 160°.

Homopiperonoylhomopiperonylamine,

$$CH_2O_2:C_6H_3·CH_2·CH_2·NH·CO·CH_2·C_6H_3:CH_2O_2,$$

m. p. 119°, is prepared from the amine and homopiperonylic acid at 160° for eight hours. Homopiperonylic acid is obtained in 5% yield by oxidising safrole in well-cooled acetone with potassium permanganate and treating the precipitate with sulphurous acid, whereby piperonylic acid is precipitated ; the homopiperonylic acid is extracted from the filtrate by ether.

Anhydrous oxalic acid reacts with β-phenylethylamine at 180—200° to form oxalodi-β-phenylethylamide, m. p. 186°, in 61% yield, and with homopiperonylamine at 170—180° to form *oxalodihomopiperonyl-*

amide, $C_2O_2(NH\cdot CH_2\cdot CH_2\cdot C_6H_3:CH_2O_2)_2$, m. p. 196—197° (corr.), colourless needles.

Fagaramide (Thoms and Thümen, A., 1912, i, 115) can be synthesised by heating piperonylacrylic acid and *iso*butylamine at 190—200° for two and a-half hours. C. S.

The Oxidation of Substituted Aceanthrenequinones. D. Butesou (*Ber.*, 1913, **46**, 212—214. Compare Liebermann and Butescu, A., 1912, i, 467).—The substituted aceanthrenequinones behave on oxidation in a similar manner to aceanthrenequinone itself, yielding anthraquinonecarboxylic acids (Liebermann and Zsuffa, A., 1911, i, 202). The oxidation is effected in acetic acid solution by chromic acid.

β-Methylanthraquinone-α-carboxylic acid, yellow needles, m. p. 295°, is obtained in the oxidation of β-methylaceanthrenequinone.

β-Chloroanthraquinone-α-carboxylic acid, yellow needles, m. p. 260°, obtained from β-chloroaceanthrenequinone, is distinct from the β-chloro-anthraquinonecarboxylic acid described by Heller and Schülke (A., 1908, i, 994).

α-Chloroanthraquinone-α-carboxylic acid, obtained by the oxidation of α-chloroaceanthrenequinone, forms leaflets, m. p. 205°, which can be sublimed to give yellow needles; it is distinct from the isomeric substances described by Heller and Schülke (*loc. cit.*) and Fischer and Sapper (A., 1911, i, 279).

1 : 5-*Dichloroanthraquinone-4-carboxylic acid*, obtained from 1 : 5-dichloroaceanthrenequinone, has m. p. 250°.

1 : 8-*Dichloroanthraquinone-5-carboxylic acid*, from the corresponding aceanthrenequinone, forms yellow needles, m. p. 240°. D. F. T.

Action of Magnesium on a Mixture of Allyl Bromide and Phthalic Anhydride. A. Orlov (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1868—1870. Compare Bauer, Abstr., 1904, i, 417; 1905, i, 210).

Diallylphthalide, $C_6H_4\!\!<\!\!\begin{smallmatrix}C(C_3H_5)_2\\CO\end{smallmatrix}\!\!>\!\!O$, prepared by the action of water on the product of the interaction of magnesium, allyl bromide, and phthalic anhydride, is a pale yellow, slightly mobile liquid of pleasant odour, b. p. 184—185°/14 mm., D_4^{25} 1·0546, n_D^{25} 1·53614, and develops fluorescence on prolonged keeping. It unites with 4 atoms of bromine, giving a liquid *bromide*, $C_{14}H_{14}O_2Br_4$, of pleasant odour. T. H. P.

The Reaction between 5-Bromo-2 : 4 : 6-tri-iodo-1 : 3-dinitro-benzene and Ethyl Sodiomalonate. C. Loring Jackson and F. C. Whitmore (*Ber.*, 1913, **46**, 67—70).—The explanation (Jackson and Bigelow, A., 1911, i, 101) of the reaction between ethyl sodio-malonate and halogen-nitrobenzenes in which one of the halogen atoms of the latter becomes replaced by hydrogen is now tested by applying it to 5-bromo-2 : 4 : 6-tri-iodo-1 : 3-dinitrobenzene; this substance is found, in accordance with the hypothesis, first to form with the ethyl sodio-malonate, an *additive* compound which probably has the constitution

$CO_2Et \cdot CHI \cdot C(ONa)(OEt) \cdot C_6BrI_2(NO_2)_2$, which when acidified undergoes scission into $C_6HBrI_2(NO_2)_2$ and $CHI(CO_2Et)_2$, the latter substance then reacting with a second molecule of ethyl sodiomalonate with the formation of ethyl ethanetetracarboxylate.

The additive compound could not be isolated, but a mixture of 2-bromo-1 : 3 : 5-tri-iodo-4 : 6-dinitrobenzene and ethyl sodiomalonate in alcohol gives a deep red liquid ; if an excess of the halogen compound or of ethyl sodiomalonate is taken and a little of the filtered red liquid is evaporated, the percentages of sodium in the residue in the former case and of halogen in the latter are in accord with the above composition.

The direct coupling of the substituted benzene ring with the ethyl sodiomalonate is attributed to the possibility that the substituted ring is more negative than the iodine atom, and it is held that the formation of *p*-toluenesulphinic acid and ethyl ethanetetracarboxylate from *p*-toluenesulphonyl chloride and ethyl sodiomalonate (Kohler and MacDonald, A., 1899, i, 907) is in support of such a view.

D. F. T.

Polymerisation of Cinnamylideneacetic Acid by Light. C. N. RIIBER (*Ber.*, 1913, 46, 335—338).—The author has obtained the dimolecular form of cinnamylideneacetic acid by the action of light on cinnamylideneacetic acid.

Cinnamylideneacetic acid was exposed to the action of light until the product had a mean mol. wt. of about 260 in acetone. The complex mixture so obtained was treated with a large quantity of benzene, whereby considerable quantities of oxidation products were isolated. The residue obtained by evaporation of the benzene mother liquor, after successive treatment with cold and boiling benzene, left a white, crystalline residue of *bimolecular cinnamylideneacetic acid*, needles, m. p. 219°, mol. wt. in acetone solution 320, which was purified by solution in methylal and addition of benzene. The acid is very sparingly soluble in the usual solvents. The *silver* salt was

examined. The formula $\begin{array}{c} Ph \cdot CH \cdot CH \cdot CH : CH \cdot CO_2H \\ | \\ CO_2H \cdot CH \cdot CH \cdot CH : CHPh \end{array}$ is assigned to

the acid, since when oxidised by potassium permanganate in alkaline solution, it yielded oxalic and benzoic acids, and an *acid* which could not be obtained in the pure state but gave a *silver* salt, $C_{13}H_9O_6Ag_3$, and a *methyl* ester, $C_{16}H_{18}O_6$. Since it was stable towards potassium permanganate, its composition is probably represented by the formula

$$\begin{array}{c} Ph \cdot CH \cdot CH \cdot CO_2H \\ | \\ CO_2H \cdot CH \cdot CH \cdot CO_2H \end{array}$$

*allo*Cinnamylideneacetic acid is similarly, but more readily, polymerised by the action of light.

Bimolecular cinnamylideneacetic acid (m. p. 219°) differs greatly from the isomeric acid (m. p. 204°) obtained by the action of light on cinnamylidenemalonic acid (A., 1902, i, 617), particularly in regard to solubility in acetone. The latter acid, when oxidised by potassium permanganate, yielded benzoic and oxalic acids, together with a saturated *acid*, m. p. 134°. α-Truxillic acid could not be isolated. The formula

$$Ph \cdot CH \cdot CH \cdot CH \colon CH \cdot CO_2H$$
$$CO_2H \cdot CH \colon CH \cdot CH \cdot CHPh$$ is advanced for the acid m. p. 204°.

<div align="right">H. W.</div>

New Oxime of Santonin. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 796—800).—When nitrosohydroxylamino-β-santoninoxime (Francesconi and Cusmano, A., 1909, i, 724) is heated with an equimolecular quantity of N-sodium hydroxide on the water-bath, nitrous oxide is evolved, and an oxime is formed, which is identical with the santoninoxime of Cannizzaro (A., 1886, 73). If, however, nitrosohydroxylamino-a-santoninoxime is similarly treated, a new *santoninoxime* of the same composition is produced; it differs from Cannizzaro's oxime in physical and to a certain extent in chemical properties, and is regarded by the author as representing the oxime of formula II, which is stereoisomeric with the oxime of formula I (Cannizzaro's oxime), adopting the formulæ deduced from the work of Angeli and Marino (A., 1907, i, 321).

<div align="center">(I.)   (II.)</div>
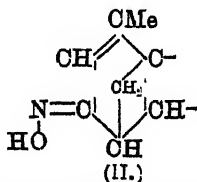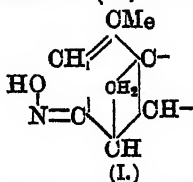
The new oxime crystallises with $1\frac{1}{2}H_2O$, in scales or in lustrous needles; on heating, it becomes red towards 180°, m. p. 230° (decomp.). In addition this a-oxime differs from the β-oxime of Cannizzaro in having a bitter taste, and in yielding the corresponding *santoninic acid*, $C_{15}H_{21}O_4N,3\frac{1}{2}H_2O$, m. p. 80°, when its solution in sodium hydroxide is exactly precipitated with acid. If this acid is kept at 100° for twenty hours, the original oxime is formed. The *hydrochloride* of the oxime crystallises in colourless scales, which change on keeping into large prisms; on heating, the hydrochloride undergoes gradual change until it melts at 168°. With water it yields the oxime, together with santonin and hydroxylamine hydrochloride.

When treated with sodium nitrite and acetic acid, the new oxime yields a *pernitroso*-derivative, $C_{15}H_{18}O_4N_2,H_2O$, which forms prismatic crystals, which become red at 175°, m. p. 197° (with evolution of gas). This compound differs from that obtained from the other oxime in m. p. and in water of crystallisation, but resembles it in giving santonin when heated with alkali, and yielding a blue coloration with a solution of diphenylamine in sulphuric acid.

Treatment of the β-oxime with methyl sulphate yields a *monomethyl ether*, $C_{16}H_{23}O_4N$ (which forms silky, acicular crystals, m. p. 184°), and also another *substance* having the same composition, but crystallising in long, thin needles, m. p. 196°.

Under the same conditions the a-oxime gives a *methyl ether* of the same composition, which forms large, prismatic crystals, m. p. 185°. A mixture of this ether with that of m. p. 184° has m. p. about 160°.

<div align="right">R. V. S.</div>

The Action of Oxalyl Chloride on Polynuclear Hydrocarbons. CARL LIEBERMANN and M. KARDOS (*Ber.*, 1913, **46**, 198—212. Compare A., 1911, i, 202, 387, 656; 1912, i, 464).— 2 : 4 : 2′ : 4′-Tetramethyldiphenyl, when oxidised by prolonged boiling with sodium dichromate and diluted sulphuric acid, gives in poor yield diphenyl-2 : 4 : 2′ : 4′-tetracarboxylic acid (compare Liebermann and Kardos, A., 1912, i, 465); the same acid is obtained with still more difficulty by the oxidation of 2 : 7-dimethylphenanthraquinone, in which phenanthraquinone-2-carboxylic acid can be isolated as an intermediate product.

Oxalyl chloride reacts with 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethyldiphenyl at the ordinary temperature in carbon disulphide solution in the presence of aluminium chloride, giving a mixture of 1 : 2 : 4 : 5 : 7 : 8-*hexamethylphenanthra*-9 : 10-*quinone*, yellow prisms, m. p. 223—224° (the *monoxime*, yellow flakes, m. p. 178°, when submitted to the Beckmann rearrangement gives a *substance*, possibly the mononitrile of hexamethyldiphenic acid; the *monophenylhydrazone* exists in two forms, *α*- red needles, m. p. 187°, *β*- yellow needles, m. p. 143°, which are possibly *cis*- and *trans*-isomerides respectively), with 2 : 4 : 5 : 2′ : 4′ : 5′-*hexamethyldiphenyldicarboxylic acid*, a microcrystalline powder, m. p. 284—285°, which is turned yellow by light. This acid when oxidised in alkaline solution by potassium permanganate is converted into *diphenyl*-2 : 4 : 5 : 2′ : 4′ : 5′ : ? : ?′-*octacarboxylic acid*, a hygroscopic solid which gives a fluorescein reaction when fused with resorcinol ; *calcium* salt, very soluble ; *silver* salt, colourless ; when dried at 110°, the acid loses carbon dioxide and water, giving the *monoanhydride* of *diphenylhexacarboxylic acid*, $C_{12}H_4(CO_2H)_4 <^{CO}_{CO}> O$; the *silver* salt was prepared.

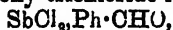3 : 4 : 5 : 3′ : 4′ : 5′-Hexamethyldiphenyl was prepared from 5-aminohemimellithene (Noelting and Forel, A., 1886, 58 ; Limpach, A., 1888, 464); in the preparation of this latter substance by heating a mixture of *s*-xylidine hydrochloride and methyl alcohol at 250—260° under 30—33 atmospheres' pressure, a relatively large quantity of acridine bases was obtained as a high boiling, feebly basic mixture, which gave fluorescent solutions in organic solvents ; there could be isolated from this mixture a *substance*, m. p. 223°, another substance (probably *tetramethylacridine*), m. p. 172—175°, and a *hexamethylacridine*, m. p. 220—225°; *hydrochloride*, yellow ; *platinichloride*, yellow and sparingly soluble. Aminohemimellithene was converted through the corresponding diazonium salt into 5-*iodohemimellithene*, crystals, m. p. 35°, which on heating with finely divided copper (compare Ullmann, A., 1904, i, 725) at 230—250°, loses iodine with the formation of 3 : 4 : 5 : 3′ : 4′ : 5′-*hexamethyldiphenyl*, m. p. 132—133°. In an experiment on a small scale, in which hexamethyldiphenyl and oxalyl chloride were kept for six weeks in carbon disulphide solution in contact with aluminium chloride, the product was a mixture of carboxylic acids with a neutral yellow *substance*, doubtless the expected 1 : 2 : 3 : 6 : 7 : 8-hexamethylphenanthra-9 : 10-quinone.

In extension of the earlier result with phthalic acid which was converted by acetyl chloride into phthalyl chloride (Liebermann, A.,

1912, i, 464), it is found that terephthalic and *iso*phthalic acids in like manner with acetyl chloride at 130° give *terephthalyl chloride*, needles or leaflets, m. p 83—84° (compare Schreder, this Journ., 1874, 990), and *iso*phtha*lyl chloride*, prisms, m. p. 43—44°, respectively; in the former case the product is accompanied by a little *terephthalyl acid chloride*, $C_6H_4 \cdot COCl \cdot CO_2H$, needles, m. p. above 300°.   D. F. T.

Compounds of Benzaldehyde and Benzonitrile with Antimony Trichloride and Tribromide. BORIS N. MENSCHUTKIN (*J. Russ Phys. Chem Soc*, 1912, **44**, 1929—1938. Compare A., 1912, ii, 920, and *ante*)—For benzaldehyde, Haase (A., 1893, ii, 357) gave the m. p. − 26°, and Altschul and von Schneider (A., 1895, ii, 206) − 13·5°. The author finds that different preparations of the aldehyde melt at temperatures varying from − 26° to − 15°. This behaviour is probably due to the ready oxidisability of the aldehyde in the air, most samples containing dissolved peroxide and acid. With the systems containing benzaldehyde, difficulties were encountered in determining temperatures lying between the melting point of the aldehyde and the first eutectic point.
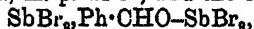
Benzaldehyde and antimony trichloride form the compound
$$SbCl_3,Ph \cdot CHO,$$
m. p. 43·5°, crystallising in elongated plates, often united in stellar aggregates. The eutectic point between this compound and the pure trichloride lies at 25°, and corresponds with the composition
$$SbCl_3,0 \cdot 44Ph \cdot CHO.$$
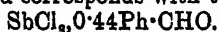
The compound $SbBr_3,Ph \cdot CHO$ forms rhombic plates and crystals resembling rhombohedra, m. p. 41·5°, and the eutectic point,
$$SbBr_3,Ph \cdot CHO-SbBr_3,$$
lies at 37·8°, and corresponds with the composition
$$SbBr_3,0 \cdot 63Ph \cdot CHO.$$
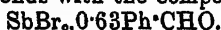
Benzonitrile has m. p. − 13·2° (Hofmann, *Jahresbericht*, 1862, 335, gave − 17°, and von Schneider, A., 1896, ii, 290, and 1897, ii, 304, − 12·9°).

The compound $SbCl_3,Ph \cdot CN$ crystallises in quadratic plates, m. p. 21·5°, and the eutectic temperatures and compositions of the system are (1) for $Ph \cdot CN-SbCl_3,Ph \cdot CN$, − 19° and $SbCl_3,10 \cdot 6Ph \cdot CN$, and (2) for $SbCl_3,Ph \cdot CN-SbCl_3$, − 15° and $SbCl_3,0 \cdot 59Ph \cdot CN$.

The compound $SbBr_3,Ph \cdot CN$ forms long plates or needles, m. p. 38°, and the eutectic points are 18° for $SbBr_3,8 \cdot 7Ph \cdot CN$ and 35° for
$$SbBr_3,0 \cdot 74Ph \cdot CN.$$
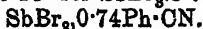
The diagrams of all the above systems have the form typical of the formation from the components of a single stable compound.   T. H. P.

New Synthesis of Syringaldehyde. FERDINAND MAUTHNER (*Annalen*, 1913, **395**, 273—281).—Syringaldehyde is readily obtained in good yield by Guyot's process (A., 1909, i, 935; 1910, i, 40) A mixture of pyrogallol 1 : 3-dimethyl ether, ethyl mesoxalate, anhydrous zinc chloride, and a little carbamide is kept in glacial acetic acid for fourteen days, whereby *ethyl 4-hydroxy-3 : 5-dimethoxyphenyltartronate*, $OH \cdot C_6H_2(OMe)_2 \cdot C(CO_2Et)_2 \cdot OH$, m. p. 60°, is obtained in almost

quantitative yield. The ester, by hydrolysis by boiling aqueous potassium hydroxide, acidification below 10°, and treatment with aqueous copper sulphate finally at the b. p., is converted into 4-*hydroxy*-3 : 5-*dimethoxyphenylglyoxylic acid* (*syringoylcarboxylic acid*),

$$OH \cdot C_6H_2(OMe)_2 \cdot CO \cdot CO_2H,$$
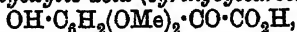
m. p. 128—129°, yellow needles (p-*nitrophenylhydrazone*, m. p. 225° [decomp.], yellow needles), which yields syringaldehyde by treatment with boiling dimethyl-*p*-toluidine as in Guyot's method. The relative positions of the aldehydo- and hydroxyl groups in the aldehyde are proved by the fact that it yields gallaldehyde trimethyl ether by treatment with methyl sulphate in alkaline solution.

Syringaldehyde forms a p-*nitrophenylhydrazone*, m. p. 216—217°, yellow needles, and an *aldazine*, $C_9H_{12}O_3N_2$, m. p. 208—209°, yellow needles, and reacts with 1-phenyl-3-methyl-5-pyrazolone in hot glacial acetic acid to form 1-*phenyl*-4-p-*hydroxydi*-m-*methoxybenzylidene*-3-*methyl*-5-*pyrazolone*, $C_{19}H_{18}O_4N_2$, m. p. 208—209°, red leaflets, with acetophenone and 33% sodium hydroxide in alcohol at 80° to form, after acidification, 4-*hydroxy*-3 : 5-*dimethoxybenzylidenebisacetophenone*, $C_{25}H_{24}O_5$, m. p. 112—113°, faintly yellow leaflets, and with β-naphthylamine and pyruvic acid in boiling alcohol to form a-p *hydroxydi*-m-*methoxyphenyl*-β-*naphthacinchonic acid*, $C_{22}H_{17}O_5N$, m. p. 275° (decomp.), yellow needles.   C. S.

a-Chloro*cyclo*pentanone and its Derivatives. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1913, **156**, 332—334).—By passing dry chlorine over *cyclo*pentanone kept at a temperature below 25°, a mixture of substances is obtained, which on fractionation yields 2-*chloro*cyclo*pentanone*, C_5H_7OCl, b. p. 80°/10 mm., D_{14} 1·870, n_D^{14} 1·4782, which on boiling with water or an aqueous suspension of barium carbonate is converted into cyclo*pentanone*-2-*ol*, $C_5H_8O_2$, b. p. 80°/12 mm, D 1·1680. It is very soluble in water, and in solution gives a reddish-brown colour with potassium hydroxide and a violet-red with ferric chloride. It forms a *phenylhydrazone*, yellow needles, m. p. 142—143°, and a *semicarbazone*, a yellow powder decomposing at 170°. This hydroxy-ketone is readily oxidised by 1% potassium permanganate to glutaric acid.

On distilling 2-chloro*cyclo*pentanone either alone or, better, with diethylaniline, it loses hydrogen chloride and is converted into Δ^2-*cyclo*pentenone, a colourless liquid, b. p. 135—136°, which gives a *semicarbazone*, m. p. 214—215°, and an *oxime*, m. p. 52—53°.
                                                                    W. G.

Terpenes and Ethereal Oils. CXIII. Autoreduction of Hydroaromatic Compounds at the Moment of their Formation. OTTO WALLACH and PAUL FRY (*Annalen*, 1913, **395**, 74—86).—β-Methyl-Δ^β-hepten-ζ-one and zinc chloride form at the ordinary temperature after two to three weeks a very viscous, brown mass which is probably an additive compound, since it is decomposed into its generators by water. At 100°, however, methylheptenone reacts vigorously in the presence of zinc chloride or phosphoric oxide; hydrogen is not evolved and the product is a complex mixture from

which an oil is obtained by distillation with steam. By distillation this oil yields a very large fraction, b. p. 130—140°, which is not 1 : 3 dimethyl*cyclo*-Δ^1 ^{3}-hexadiene as stated previously, but is proved to be a mixture of *m*-xylene and 1 : 3-dimethyl-Δ^1-*cyclo*hexene by treatment with 3% potassium permanganate at 0°, whereby the *m*-xylene is unattacked, whilst the 1 : 3-dimethyl*cyclo*hexene is converted into 1 : 3-*dimethylcyclohexane*-3 : 4-*diol*, $OH \cdot CMe < ^{CH(OH) \cdot CH_2}_{CH_2 - CHMe} > CH_3$, m. p. 89°. The constitution of the glycol is proved by the fact that it yields 1 : 3-dimethyl*cyclo*hexan-4-one, b. p. 179—179·5°, D^{21} 0 9066, n_D^{21} 1·4464 (*semicarbazone*, m. p. 189° ; *oxime*, m. p. 98—99°), by treatment with warm dilute sulphuric acid. This ketone in an impure state (b. p. 176 5°, D^{16} 0·9124, n_D 1·446) has been described by Sabatier and Mailhe, in 1906. By oxidation with chromic and dilute sulphuric acids on the water-bath, it yields a keto-acid (*semicarbazone*, m. p. 136—137°), which is converted into bromoform and β-methyladipic acid by alkaline hypobromite.

Since hydrogen is not evolved and 1 : 3-dimethyl-Δ^1 ^{3}-*cyclo*hexadiene is not obtained by the auto-condensation of the methylheptenone, it follows that one molecule of 1 : 3-dimethyl*cyclo*hexadiene loses hydrogen and changes to *m*-xylene, the hydrogen converting a second molecule into 1 : 3-dimethyl*cyclo*-Δ^3-hexene.   C. S.

Synthetic *p*-Dialkylated Dihydroxyquinones and Hydroxy-perezone. Fritz Fichter, Max Jetzer, and Robert Leepin (*Annalen*, 1913, **395**, 1—25. Compare A., 1904, i, 678 ; 1908, i, 658).—The following substances have been prepared by the reaction, as described previously, between sodium, ethyl oxalate, and a fatty ester in ether or benzene. The reaction proceeds more slowly the greater the molecular weight of the fatty acid, and reaches its limit with *n*-decoic ester ; ethyl laurate or palmitate do not yield a *p*-dialkylated dihydroxy-quinone. 3 : 6-*Dihydroxy*-2 : 5-*diisobutyl-p-benzoquinone*, $C_{14}H_{20}O_4$, m. p. 217—218° (in closed tube), red spangles (*diacetate*, m. p. 113·5°, yellow crystals), from ethyl *iso*hexoate, develops a blue coloration in concentrated sulphuric acid and a violet in aqueous sodium hydroxide. 3 : 6-*Dihydroxy*-2 : 5-*diamyl-p-benzoquinone*, $C_{16}H_{24}O_4$, m. p. 164°, red leaflets (*diacetate*, m. p. 74°, yellow needles), from ethyl *n*-heptoate ; 3 : 6-*dihydroxy*-2 : 5-*dihexyl-p-benzoquinone*, $C_{18}H_{28}O_4$, m. p. 154°, red scales (*diacetate*, m. p. 68°, yellow needles), from ethyl *n*-octoate ; 3 : 6-*dihydroxy*-2 : 5-*diheptyl-p-benzoquinone*, $C_{20}H_{32}O_4$, m. p. 145°, red leaflets (*diacetate*, m. p. 77·5°, yellow needles), from ethyl *n*-nonoate ; 3 : 6-*dihydroxy*-2 : 5-*dioctyl-p-benzoquinone*, m. p. 141°, red leaflets, from ethyl *n*-decoate. In the colour of their solutions and of their alkali salts, and in their inactivity towards hydroxylamine and ortho-diamines, *p*-dialkylated dihydroxybenzoquinones show a greater similarity to chloroanilic acid than to the unsubstituted dihydroxybenzoquinone. The same is true of their ethers ; 3 : 6-*dimethoxy*-2 : 5-*diisopropyl-p-benzoquinone*, $CPr^\beta < ^{C(OMe) \cdot CO}_{CO \cdot C(OMe)} > CPr^\beta$, m. p. 142°, prepared from the silver derivative, crystallises in almost black leaflets.

Ethyl iso*valerylacetate*, $CH_2Pr^\beta \cdot CO \cdot CH_2 \cdot CO_2Et$, b. p. 99·5°/12·5 mm.,
D^{15} 0·964, prepared by hydrolysing ethyl *iso*valerylacetoacetate with
aqueous ammonia, is soluble in alkalis, develops an intense red colora-
tion with ferric chloride, yields 1-*phenyl*-3-iso*butyl*-5-*pyrazolone*,

$$CH_2Pr^\beta \cdot C \underset{N---NPh}{\overset{CH_2 \cdot CO}{<}},$$
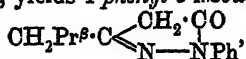
m. p. 105·5°, with phenylhydrazine, and condenses with resorcinol and
concentrated sulphuric acid to form 5-*hydroxy*-4-iso*butylcoumarin*,
$C_{13}H_{14}O_3$, m. p. 117°, glistening needles, which dissolves in alkalis with
a blue fluorescence.

By treatment with ozonised oxygen, 3 : 6-dihydroxy-2 : 5-dialkyl-
p-benzoquinones in dry chloroform at 0° do not yield ozonides,
but are decomposed in the sense of the equation :

$$C_6R_2(OH)_2O_2 + 6O + 2H_2O = 2H_2C_2O_4 + 2R \cdot CO_2H,$$
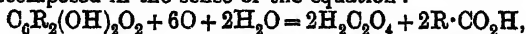
the necessary water being produced by the complete oxidation of
a portion of the quinone ; thus dihydroxydi*iso*propyl-*p*-benzoquinone
yields oxalic and *iso*butyric acids, dihydroxy-*p*-xyloquinone yields oxalic
and acetic acids (the same products are also obtained by the oxidation
of the quinone by alkaline potassium permanganate), dihydroxy-
diethyl-*p*-benzoquinone yields oxalic and propionic acids, and dihydroxy-
thymoquinone yields oxalic and *iso*butyric acids, acetic acid not being
detected.

The study of dialkylated dihydroxybenzoquinones has thrown con-
siderable light on the constitution of perezone (pipitzahoic acid). This sub-
stance is converted through the anilino-derivative into hydroxyperezone
by Mylius's method (A , 1885, 777, 805). Hydroxyperezone, $C_{15}H_{20}O_4$,
m. p. 138—139°, yellowish-red needles, resembles the dialkylated
dihydroxy-*p*-benzoquinones in its colour, in the colorations it develops
with concentrated sulphuric acid and with aqueous sodium hydroxide
respectively, and in its conversion into a *tetra-acetate*, $C_{23}H_{30}O_8$, m. p.
97—98°, colourless crystals, by reductive acetylation. By treatment
in chloroform with ozonised oxygen, it yields oxalic acid and not
a volatile fatty acid as expected, but $\alpha\beta$-diketobutyric acid, which is
isolated and identified by treating its aqueous solution with phenyl-
hydrazine, whereby $\alpha\beta$-diketobutyric acid phenylosazone (completely
identified by its conversion by warm alkali into 4-benzeneazo-1-phenyl-
3-methyl-5-pyrazolone) is obtained. The formation of the diketo-
butyric acid is accounted for if one of the side-chains in hydroxy-
perezone is a propenyl group. Consequently, the other side-chain must
be a hexyl group, since the sum of the carbon atoms in the side-chains
is 9. Hydroxyperezone, therefore, has the constitution

$$C_6H_{13} \cdot C \underset{CO \cdot C(OH)}{\overset{C(OH) \cdot CO}{<}} > C \cdot CH{:}CHMe.$$
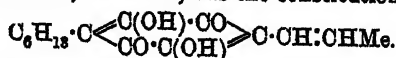
Since hydroxyperezone readily loses water to form perezinone (Mylius,
loc. cit.), whilst perezone does not suffer an analogous change, perezone
has the constitution $C_6H_{13} \cdot C \underset{CO---CH}{\overset{C(OH) \cdot CO}{<}} > C \cdot CH{:}CHMe$, and pere-
zinone is $\underset{C(C_6H_{13}) \cdot CO \cdot C \cdot CH_2}{\overset{C(OH)---CO \cdot C---CH}{|}} > CH.$ By reduction with sodium
amalgam and aqueous sodium hydroxide at 100°, hydroxyperezone yields

hexylpropenyldihydroresorcinol, $C_{15}H_{24}O_2$, m. p. 140—144°, colourless needles. By similar treatment, dihydroxythymoquinone yields *methyl-isopropyldihydroresorcinol*, $C_{10}H_{16}O_2$, m. p. 170°, softening at 145°, colourless leaflets. C. S.

Camphor and its Derivatives. XII. JULIUS BREDT (*Annalen*, 1913, **395**, 26—63).—[With J. HOUBEN, P. LEVY, and S. LINK.]—

Methyl 4-chlorocamphorate, $\begin{matrix} CH_2-CCl(CO_2Me) \\ CH_2 \cdot CMe(CO_2Me) \end{matrix} > CMe_2$, m. p. 56°, b. p.

158°/15 mm., is prepared from 4-chlorocamphoryl chloride and sodium methoxide in methyl alcohol. By slow distillation at 254—285° under ordinary pressure, it yields hydrogen chloride and *methyl dehydro-camphorate*, $C_{12}H_{18}O_4$, b. p. 137°/15 mm., and also methyl chloride and methyl camphanate, the latter decomposition resembling that which occurs during the distillation of the ester of a γ-halogenated fatty acid. *Phenyl 4-chlorocamphorate*, $C_{22}H_{25}O_4Cl$, m. p. 89°, obtained in a similar manner from sodium phenoxide in petroleum (b. p. 70—100°), yields, by slow distillation or by heating with quinoline, only hydrogen chloride and *phenyl dehydrocamphorate*, $C_{22}H_{22}O_4$, m. p. 155°. *Phenyl dl-4-chloro-camphorate*, m. p. 74°, yields *phenyl* dl-*dehydrocamphorate*, m. p. 133°, by similar treatment.

By hydrolysis with aqueous methyl alcoholic potassium hydroxide, removal of the alcohol and phenol, and subsequent acidification, phenyl dehydrocamphorate yields *d*-dehydrocamphoric acid, m. p. 202—203°,

$[α]_D^{21}$ +118·6° in chloroform and +113·8° in alcohol, which is converted into iso*dehydrocamphoric an-hydride* (annexed formula), m. p. 185·5—186°, and camphonenic acid by distillation under ordinary pressure. iso*Dehydrocamphoric acid* has m. p. 181—182°, and readily yields the anhydride by treatment with cold acetyl chloride. Dehydrocamphoric acid yields camphoronic acid by oxidation with dilute nitric acid or alkaline potassium permanganate, and forms a *methyl hydrogen* ester, $C_{11}H_{16}O_4$, m. p. 96°, *silver* salt, $C_8H_{12}(CO_2Ag)_2,H_2O$, and *calcium* salt, $C_{10}H_{12}O_4Ca,4H_2O$.

It does not form an anhydride, and yields the *chloride*, $C_{10}H_{12}O_2Cl_2$, b. p. 139°/13·5 mm., m. p. about 50°, by treatment with phosphorus pentachloride or acetyl chloride. The non-formation of an anhydride and the fact that its chloride reacts with aqueous ammonia at 0° to form the *diamide*, $C_{10}H_{16}O_2N_2,H_2O$, m. p. 191°, colourless needles (compare A., 1912, i, 411), show that dehydrocamphoric acid has something approaching the *cis-trans* configuration. Reference to the tetrahedral model shows that the two carboxyl groups are in what the author terms the *meso-trans* position, in which the spatial separation of the acidic groups is almost as great as in the *cis-trans* modification of the isomeric iso*dehydrocamphoric acid*.

The non-existence of dehydrocamphoric anhydride explains why hydrogen chloride or bromide cannot be eliminated from the C_5-ring of 4-chloro- or bromo-camphoric anhydride.

With S. LINK and TH. FUSSGÄNGER.]—When heated at 100° for

six hours with hydrobromic acid saturated at 0°, *d*-dehydrocamphoric acid yields a mixture of cis-3-*bromocamphoric acid*, m. p. 158—160°, and trans-3-*bromocamphoric acid*, m. p. 232°, of which the former is easily soluble in benzene. The *cis*-acid, which is the chief product of the action of hydrobromic acid at 0°, yields *cis*-camphoric acid, and the *trans*-acid yields *trans*-camphoric acid, by reduction with zinc and glacial acetic and 24% hydrochloric acids. The action of hydrobromic acid at 100° on *dl*-dehydrocamphoric acid yields a mixture of two stereoisomeric dl-3-*bromocamphoric acids*, m. p. 188—189° (decomp.) and 239—240° respectively, of which the less fusible is the chief product, is insoluble in benzene, and yields *trans-dl*-camphoric acid by reduction. Unlike the active acid, *dl*-dehydrocamphoric acid is not attacked by hydrobromic acid at 0°, even after three months.

By boiling with aqueous sodium carbonate and subsequently acidifying, *cis*-3-bromocamphoric acid yields 3-*hydroxycamphorolactone*, $C_{10}H_{14}O_4$, m. p. 228°, whilst *trans*-3-bromocamphoric acid yields trans-3-*hydroxycamphoric acid*, $C_{10}H_{16}O_5$, m. p. 194°, and camphonenic acid, m. p. 155°, identical with that mentioned above and with the un-saturated acid obtained by Noyes from the nitroso-derivative of aminolauronolic anhydride (A., 1906, i, 397). The constitution of camphonenic acid is proved by the formation of camphoronic acid by oxidation with nitric acid or potassium permanganate.

3-Hydroxycamphorolactone boils unchanged, but *trans*-3-hydroxycamphoric acid yields dehydrocamphoric acid and *iso*dehydrocamphoric anhydride by slow distillation. *trans*-3-Hydroxycamphoric anhydride yields only the latter by distillation.

By heating equal molecular quantities of bromine and dehydro-camphoryl chloride at 100° for six hours, decomposing the product with aqueous sodium carbonate, and acidifying, an unsaturated *acid*, $C_9H_{12}O_2$, m. p. 149°, colourless needles, is obtained, which is probably *dehydrolaurolenic acid*.

From the behaviour of the two acids, it is probable that in *cis*-3-bromocamphoric acid the two carboxyl groups are each in the *cis*-position to the bromine atom, whilst in *trans*-3-bromocamphoric acid the bromine is in the *cis*-position to the neighbouring carboxyl and in the trans-position to the other carboxyl group, because lactone formation does not occur by the distillation of its esters, although the halogen is in the γ-position to the carboxyl group.   C. S.

Action of Magnesium and Allyl Haloids on Camphor. METSCHISLAV CHOJN (*J. Russ. Phys. Chem. Soc.* 1912, 44, 1844—1853). —*Allylborneol* (1 : 7 : 7-*trimethyl*-2-*allyl*-1 : 2 : 2-bicyclo*heptan*-2-*ol*),
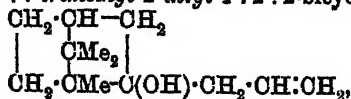
$$CH_2 \cdot CH = CH_2$$
$$| \quad CMe_2 |$$
$$CH_2 \cdot CMe \cdot C(OH) \cdot CH_2 \cdot CH{:}CH_2,$$

obtained by decomposing with water the product of the interaction of magnesium, allyl bromide or iodide, and camphor, is a colourless, viscous liquid with a pleasant camphor-like odour, b. p. 118—119°/17 mm., 120—121°/21 mm., D_4^{18} 0·9474, n_D^{18} 1·48943, and exhibits the normal molecular weight in freezing benzene or boiling ether. It

unites with two atoms of bromine and, when treated in ethereal solution and in presence of anhydrous sodium sulphate with dry hydrogen chloride at 0°, gives the analogous chloro-derivative, which is converted into the corresponding unsaturated hydrocarbon when heated with dry pyridine.

Oxidation of allylborneol with 1% potassium permanganate solution yields *βγ-dihydroxypropylborneol* (1 : 7 : 7-*trimethyl-2-propan-βγ-diol-*

$$CH_2 \cdot \overset{|}{C}H-CH_2$$

1 : 2 : 2-bicyclo*heptan*-2-*ol*), $\overset{|}{C}Me_2 \overset{|}{}$,

$$CH_2 \cdot CMe \cdot C(OH) \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$$
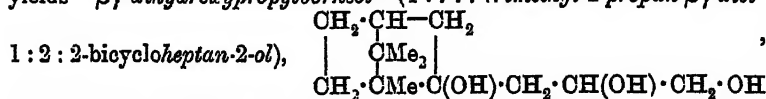
which forms radiating or beard-like masses of tasteless, odourless, snow-white crystals, m. p. 119—120°, and exhibits normal ebullioscopic behaviour in benzene.
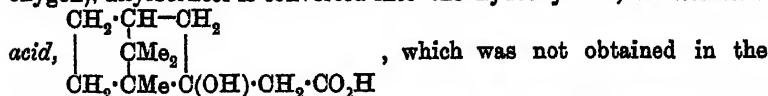
When oxidised with 4% potassium permanganate (4 atoms of oxygen), allylborneol is converted into the hydroxy-acid, *borneolacetic*

$$CH_2 \cdot \overset{|}{C}H-CH_2$$

acid, $\overset{|}{C}Me_2 \overset{|}{}$, which was not obtained in the

$$CH_2 \cdot CMe \cdot C(OH) \cdot CH_2 \cdot CO_2H$$

pure state; the *ammonium*, *silver*, and *calcium* ($+2H_2O$) salts of the acid were prepared and analysed.   T. H. P.

Bupleurol. The Alcohol from the Essential Oil of Bupleurum fructicosum. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 34—40).—This alcohol, which the authors named *bupleurol*, can be isolated by the aid of phthalic anhydride from the higher fractions of the essential oil. It has the composition $C_{10}H_{20}O$, b. p. 209—210°/762 mm., D^{17} 0 8490, n_D 1·4508, and is optically inactive; the substance has a slight, pleasant odour of roses. From its physical properties the substance is probably an olefinic alcohol, and this is supported by the fact that it yields an oily *dibromide*. It forms a *urethane*, which crystallises in lustrous needles, m. p. 45°. Oxidation of bupleurol with chromic acid yields: (1) an *aldehyde*, which shows Schiff's reaction, and gives a *semicarbazone*, m. p. 135°; (2) an *aldehyde*, of which the *semicarbazone* has m. p. 97°; (3) a *ketone* (b. p. 217°, n_D^{25} 1·4419), which yields a *semicarbazone*, m. p. 189—190°; (4) a red oil, b. p. 207°, which is the *ester* of bupleurol and the corresponding *acid*, which was also isolated. Bupleurol is isomeric with citronellol and with androl, and the authors assign to it the formula $CHMe_2 \cdot [CH_2]_3 \cdot C(CH_2) \cdot CH_2 \cdot CH_2 \cdot OH$, which is that of a dihydro-derivative of nerol.

When the *phthalic* ester of bupleurol is dissolved in ammonia and treated with silver nitrate, the *silver* salt, $C_{18}H_{28}O_4Ag$, is obtained, m. p. 135°.

In the isolation of bupleurol, a *substance*, $C_{10}H_{16}O$, is also met with; it has an acrid odour, gives a coloration with Schiff's reagent, reduces ammoniacal silver nitrate, and has D 0·9264, $[a]_D$ 14·93°, n_D 1·4909.
                                               R. V. S.

Insoluble Constituents of Ceara- and Rambong-Caout-chouc. CLAYTON BEADLE and HENRY P. STEVENS (*Zeitsch. Chem. Ind.*

Kolloide, 1913, 12, 46—48).—The influence of the insoluble constituents on the properties of Ceara- and Rambong-caoutchouc has been investigated, and the results compared with those of similar experiments carried out previously with Hevea-caoutchouc (A., 1912, i, 789). "Benzine" was added to the caoutchouc, and the products recovered from the upper clear solution and the lower turbid solution were separately examined, the latter containing practically the whole of the insoluble constituent. The data compared are the nitrogen content, the proportion of free and fixed sulphur in the vulcanised material, and the mechanical properties. Although the relationships involved are of a complicated character, it would appear that the insoluble constituents play an important part in connexion with the vulcanisation of the caoutchouc, and are more or less independent of the percentage content of nitrogenous substances in the caoutchouc.   H. M. D.

Artificial Caoutchoucs. II. CARL D. HARRIES (*Annalen*, 1913, 395, 211—264).—Replies are given to the remarks of Lebedev (A., 1911, i, 959), Kondakov, Ostromisslenski, and Perkin (A., 1912, i, 636) in connexion with the author's first paper (A, 1911, i, 798).

[With MAX HAGEDORN.]—The identity of natural and of artificial caoutchoucs cannot be satisfactorily tested by a comparison of their derivatives except in the case of the ozonides. The products of their decomposition contain similar amounts of lævualdehyde and its acid and diperoxide. Also the comparison of the velocity of decomposition, under proper conditions, of the diozonides and dioxozonides (Harries and Neymann, A., 1908, i, 967; Harries, A., 1912, i, 706) gives satisfactory results. The decomposition curves of the diozonides of Para caoutchouc (purified by twice precipitating its benzene solution by alcohol, and by two extractions with acetone in a Soxhlet apparatus for twelve hours), of gutta-percha, and of artificial caoutchouc obtained by the autopolymerisation of isoprene at 95°, are the same; the decomposition curve of artificial caoutchouc, obtained from isoprene by the acetic acid process, is slightly different. The decomposition curve of "sodium" caoutchouc diozonide is quite different. The same is true of the butadiene caoutchoucs. "Sodium" butadiene-caoutchouc (purified by the alcohol-benzene method) forms a diozonide, the decomposition products of which do not contain a trace of succindialdehyde or lævulaldehyde, and the decomposition curve of which is quite different from that of the diozonide of butadiene-caoutchouc polymerised by heat.

Like natural caoutchouc, artificial "normal" caoutchoucs form diozonides and dioxozonides. Artificial "sodium" caoutchoucs also form diozonides and dioxozonides, although with greater difficulty; the products of their decomposition by water are similar, but the diozonides yield a larger proportion of aldehydes, the dioxozonides a larger amount of acids.

Gutta-percha, purified by alcohol and chloroform and by prolonged extraction with acetone, yields, with washed 9—10% ozone, a *diozonide*, $C_{10}H_{16}O_6$, which so closely resembles the diozonide of natural or of artificial caoutchouc that most probably they are identical. By further treatment with 18% ozone in chloroform, gutta-percha diozonide yields

a *dioxozonide*, $C_{10}H_{16}O_8$, which behaves like the dioxozonide of Para caoutchouc.

The authors have been able to account for a phenomenon which has frequently been observed. Caoutchouc diozonides, prepared apparently in the same manner, frequently yield, by decomposition with water, different amounts of the crystalline lævulaldehyde diperoxide, m. p. 196°; it has now been shown that the quantity of this product increases with amount of dioxozonide in the diozonide.
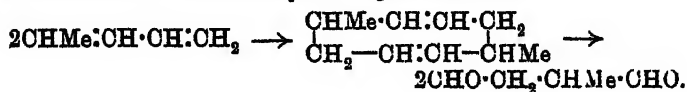
In partial agreement with Gottlob (A., 1908, i, 436), the authors find that the diozonides of African (Congo) caoutchoucs yield quantities of decomposition products distinctly different from those of the decomposition products of the diozonides of Para caoutchouc, artificial caoutchouc, and gutta-percha. Congo caoutchoucs yield dioxozonides only with difficulty.

[With WILHELM SCHONBERG.]—The exhaustive methylation of piperidine is not a suitable method for the preparation of piperylene in quantity. It can be obtained readily as follows: (1) acraldehyde and magnesium ethyl bromide yield by the usual process the alcohol, CH_2:$CH\cdot CHEt\cdot OH$, which is then dehydrated by phthalic anhydride; (2) the alcohol, $CHEt_2\cdot OH$, prepared in the usual manner from ethyl formate and magnesium ethyl bromide, yields Δ^β-pentene by distillation with phosphoric oxide; the olefine forms a *dibromide*,

$$CHMeBr\cdot CHEtBr,$$

b. p. 65—70°/15 mm., which is converted into piperylene by the sodium carbonate process at about 600°. This is the best method.

By heating for about fourteen days at 105—110° in an atmosphere of carbon dioxide, piperylene polymerises to "normal" *piperylene-caoutchouc*, $C_{10}H_{16}$, which is elastic and very closely resembles "normal" isoprene-caoutchouc in most of its properties. It forms a *nitrosite-a*, $C_{10}H_{16}O_5N_2$ (?), decomp. 118—122°, yellow powder, insoluble in acetone or ethyl acetate, and a *nitrosite-c*, $2C_{10}H_{15}O_7N_3$, decomp., 162—164°, easily soluble in acetone or ethyl acetate, and an unstable *bromide*, $C_{10}H_{15}Br_3$ (?), decomp. 150—160°, pale yellow, amorphous powder; these three derivatives are almost indistinguishable from the corresponding derivatives of "normal" isoprene-caoutchouc. The ozonides of the two caoutchoucs, however, are quite dissimilar. By treatment with washed ozone in chloroform, piperylene-caoutchouc yields the *diozonide*, $C_{10}H_{16}O_6$, which explodes violently by heating, and exhibits the usual properties of ozonides. It forms a dioxozonide only with very great difficulty. The decomposition curve of piperylene-caoutchouc diozonide is similar to, yet quite distinct from, that of normal caoutchouc diozonide, but the decomposition products are quite different. The former diozonide does not yield lævulaldehyde, but a substance which is most probably methylsuccindialdehyde. Hence "normal" piperylene-caoutchouc (which is a true structural isomeride of "normal" caoutchouc, piperylene being $\Delta^{\alpha\gamma}$-pentadiene) is a derivative of 1:5-dimethyl-2:6-*cyclo*octadiene,

$$2CHMe\text{:}CH\cdot CH\text{:}CH_2 \longrightarrow \begin{matrix} CHMe\cdot CH\text{:}CH\cdot CH_2 \\ CH_2-CH\text{:}CH-CHMe \end{matrix} \longrightarrow$$
$$2CHO\cdot CH_2\cdot CHMe\cdot CHO.$$

During the polymerisation of piperylene by heating, a by-product is obtained in the form of a *terpene*, $C_{10}H_{16}$, b. p. 58—59°/11 mm., $D_1^{20\cdot5}$ 0·8313, $n_D^{20\cdot5}$ 1·46916, n_α 1·46620, n_γ 1·48373, which forms a crystalline *bromide*, m. p. 178°, and a white *diozonide*, $C_{10}H_{16}O_6$; the velocity of decomposition of the latter by water at 125° is very great, but definite substances could not be isolated from the products owing to lack of material.

The polymerisation of piperylene by sodium at 60° yields a "sodium" piperylene-caoutchouc which is brittle after purification; it forms a *nitrosite*, decomp. 140—145°, and a *bromide*, the analyses of which do not correspond with the formulæ of the normal compounds.

[By the AUTHOR.]—The proof of the presence of an 8-ring in "normal" caoutchoucs is of fundamental importance in the chemistry of caoutchoucs. To test this point, the velocity of decomposition of "normal" butadiene-caoutchouc diozonide has been compared with that of the diozonide of Willstätter's 1 : 5-*cyclo*octadiene. (A serious difficulty is encountered in separating the "normal" butadiene-caoutchouc from the terpenoid hydrocarbon, C_8H_{12}, obtained as a by-product during the polymerisation. Both substances form almost colourless *diozonides*, $C_8H_{12}O_6$; the diozonide of the terpenoid hydrocarbon is decomposed very rapidly by water at 125°, and the products of decomposition contain hydrogen peroxide, but do not respond to the pyrrole test.) The comparison shows that both decompose at the same rate ·(at first the "normal" butadiene-caoutchouc decomposes more rapidly, but this is probably due to the presence of a little of the easily decomposable diozonide of the terpenoid hydrocarbon), and yield practically the same amount of succindialdehyde. Since the decomposition curve of 1 : 5-*cyclo*octadiene diozonide is very characteristic, and since the decomposition products of the two diozonides are quite alike in not responding to the hydrogen peroxide test and in containing the same percentage of succindialdehyde, the statement is made with considerable confidence that "normal" caoutchoucs contain an 8-ring.

[With RICHARD SEITZ.]—Although Zelinsky and Gorsky (A., 1908, i, 619) have resolved 1-methyl-$\Delta^{2:4}$-*cyclo*hexadiene into its active forms, their method of preparing the substance does not necessarily lead to the formation of a compound of this constitution (compare Harries and Neymann, A., 1909, i, 218). The authors, therefore, have used a method similar to that by which Harries obtained pure $\Delta^{1:3}$-*cyclo*hexadiene (A., 1912, i, 343). 1-Methyl-Δ^3-*cyclo*hexene and bromine in acetic acid yield 3 : 4-*dibromo*-1-*methyl*cyclohexane, b. p. 94—95°/12 mm., which reacts with 33% alcoholic trimethylamine (2 mols.) at about 95° for twenty hours to form 1-*methyl*-Δ^1-*cyclo*hexenyl-3-trimethylammonium bromide or 1-*methyl*-Δ^3-cyclohexenyl-4-trimethylammonium bromide, $C_{10}H_{20}NBr$, m. p. 166—167°. The bromide, whichever constitution it may have, must yield 1-methyl-$\Delta^{2:4}$-*cyclo*hexadiene by treatment with water and silver oxide and subsequent distillation. The hydrocarbon agrees well in its physical constants (b. p. 100·5—101·5°, D_4^{25} 0·8252, n_α 1·46225, n_β^{25} 1·46619, n_γ 1·48519) with Zelinsky and Gorsky's compound (*loc. cit.*). By treatment with unwashed 18—20% ozone in chloroform, it yields a *diozonide*, $C_7H_{10}O_6$,

which is decomposed in ether by copper hydride, yielding probably methylsuccindialdehyde and glyoxal ; these substances, however, could not be definitely identified. C. S.

Comparative Researches on the Polymerisation Products of βγ-Dimethylbutadiene obtained Spontaneously and by Heat. CARL D. HARRIES (*Annalen*, 1913, **395**, 264—272).—[With MAX HAGEDORN.]—"Normal" βγ-dimethylbutadiene-caoutchouc, produced by heating βγ-dimethylbutadiene in a closed vessel, yields very readily the diozonide and the dioxozonide, both of which are decomposed by water, giving an almost quantitative yield of acetonylacetone. Kondakov's white, insoluble polymeride, produced by the prolonged keeping of βγ-dimethylbutadiene at the ordinary temperature, also readily forms a *diozonide*, $C_{12}H_{20}O_6$, and *dioxozonide*, $C_{12}H_{20}O_8$, by the decomposition of which by water only about 20% of acetonylacetone is produced. Also the decomposition curves of the two diozonides are very different.

By exposure to air for a few hours, Kondakov's polymeride changes to a yellow, soluble resin. This forms a *diozonide*, $C_{12}H_{20}O_6$, and *dioxozonide*, $C_{12}H_{20}O_8$, by the decomposition of which about 36% of acetonylacetone is obtained.

The author is of opinion that Kondakov's polymeride is not a true caoutchouc, and by analogy, therefore, that the caoutchouc obtained by Pickles (T., 1910, **97**, 1085) by the prolonged keeping of isoprene is not true caoutchouc. C. S.

Chlorophyll. LÉON MARCHLEWSKI (*Annalen*, 1913, **395**, 194—210).—A reply to Willstätter and Isler (A., 1912, i, 710). The author maintains his contention that Willstätter's phaeophytin is chlorophyllan under another name The heterogeneity of chlorophyllan was established by the author and Malarski (A., 1909, i, 947) before Willstätter (A., 1911, i, 393).

The proportion of the components *a* and *b* in chlorophyll is determined far more conveniently by Marchlewski and Jacobson's method (A., 1912, ii, 705) than by Willstätter and Isler's process (*loc. cit.*). C. S.

Alkaloids of Aconitum Lycoctonum. HEINRICH SCHULZE and ERICH BIERLING (*Arch. Pharm.*, 1913, **251**, 8—49).—A detailed résumé is first given of the work of Hübschmann (*Schweiz. Woch. Pharm.*, 1865, **3**, 269), Dragendorff and Spohn (A., 1885, 403), Einberg (*Diss. Dorpat.*, 1887), Dohrmann (*ibid.*, 1888), and van der Bellen (*ibid.*, 1890) on these alkaloids. The author's results extend, and to some extent confirm, those of Dragendorff and his pupils. It is shown that the alkaloids of this species differ from the typical " aconitines " in not yielding two monobasic acids on hydrolysis.

The coarsely ground roots were exhausted with 94% alcohol, the extract concentrated, and set aside to deposit sucrose, the mother liquor further concentrated, and diluted with three times its volume of water to separate resin and oil, and the filtrate, after extraction with ether to remove the last traces of oil, made alkaline with sodium

hydroxide and the liberated lycaconitine extracted with ether. The alkaline liquor was then shaken with chloroform, and the amorphous alkaloids so obtained freed from traces of lycaconitine by extraction with ether. This partly purified mixture of alkaloids was dissolved in dilute hydrochloric acid (3%), the solution treated with potassium thiocyanate in excess to remove an alkaloid giving an insoluble thiocyanate, and the filtrate made alkaline with sodium hydroxide and extracted with chloroform, which removed myoctonine.

Lycaconitine, $C_{36}H_{46}O_{10}N_2$, $[a]_D^{20}$ +42·47° in alcohol, was decolorised by means of animal charcoal, and thus obtained as a colourless powder, easily soluble in alcohol or chloroform, less so in ether; it is a weak base from which no crystalline derivatives could be prepared. On hydrolysis by water or dilute hydrochloric acid, it yields succinic acid and anthranoyl-lycoctonine. Alkalis hydrolyse it to lycoctonine and lycoctoninic acid.

Myoctonine, $(C_{36}H_{42}O_{10}N_2)_2$, $[a]_D^{20}$ +44·79° in alcohol, is a colourless, amorphous powder, soluble in alcohol or chloroform, but sparingly so in ether; the solution in alcohol fluoresces bluish-violet. No crystalline derivatives were obtained. On hydrolysis by hydrochloric acid or alkalis, it furnishes the same products as lycaconitine.

The unnamed base giving an insoluble thiocyanate was not analysed; on hydrolysis by alkalis, it also yields lycoctonine and lycoctoninic acid.

Lycoctonine, $C_{25}H_{39}O_7N,H_2O$, m. p. 131—133°, $[a]_D^{20}$ +49·64° in alcohol, crystallises in long, colourless needles from dilute alcohol, is a strong base, contains four methoxyl groups and a methylimino-group, and becomes amorphous when dehydrated by drying at 100°/40 mm. The *hydrochloride*, B,HCl,H_2O, m. p. 75° (decomp.), forms colourless prisms; the *hydrobromide*, $B,HBr,2H_2O$, has m. p. 88—89°, and the *perchlorate*, $B,HClO_4,1\frac{1}{2}H_2O$, m. p. 68—69° (decomp.), forms heavy prisms. The *methiodide*, B,MeI, m. p. 178°, forms pale yellow needles from alcohol on addition of ether, and the *methochloride aurichloride*, $B,Me,HAuCl_4$, small, heavy, yellow prisms. Lycoctonine contains at least two hydroxyl groups.

Lycoctoninic acid, $C_{11}H_{11}O_5N$, m. p. 179°, forms bright brown needles or leaflets from dilute alcohol, and appears to be succinanil-carboxylic acid (Riedel, A., 1912, i, 774).

Anthranoyl lycoctonine, $C_{32}H_{44}O_8N_2$, m. p. 154—155°, forms bright brown, glancing leaflets, is easily soluble in chloroform, but sparingly so in other solvents; the solutions fluoresce bluish-violet. The alkaloid contains four methoxyl groups and a methylimino-group. The *perchlorate*, $B,2HClO_4$, alone was obtained crystalline; it forms aggregates of colourless needles, and does not melt completely even at 235°. On hydrolysis by sodium hydroxide in alcohol, the free base yields lycoctonine and anthranilic acid. Anthranoyl-lycoctonine is probably identical with Dragendorff's "lycaconine," but as it is not analogous with the other "aconines," lycoctonine be'ng the corresponding substance in this instance, it is proposed to abandon this name.

The reactions of these alkaloids with the usual alkaloidal reagents and precipitants are tabulated in the original.

Hildebrandt reports that in doses of 0·01 gram, lycaconitine stills the

frog's heart in five hours and myoctonine in seven hours, death occurring three hours later. Lycoctonine causes paralysis after seven hours, but does not still the heart, whilst the action of the relatively insoluble anthranoyl-lycoctonine only becomes apparent after six days. When paralysis of the heart's action does not come on too quickly, all the alkaloids show the characteristic action of the aconitines on the heart. T. A. H.

ψ-Laudanine. HERMAN DECKER and THEODOR EICHLER (*Annalen*, 1913, **395**, 377—381).—The reduction of an alcoholic solution of *N*-methylnorpapaverinium phenolbetaine (Decker and Dunant, A., 1908, i, 204) by tin and concentrated hydrochloric acid on the water-bath yields the *stannochloride*, $C_{20}H_{25}O_4N,HCl,SnCl_2$, of a *base*, $C_{20}H_{25}O_4N$, m. p. 111°, which has the constitution :
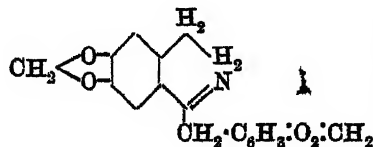
$$C_6H_3(OMe)_2 \cdot CH_2 \cdot CH < ^{C_6H_3(OH)(OMe)}_{NMe\text{———}CH_2} > CH_2,$$
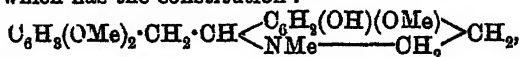
and is called *ψ-laudanine*, since it differs from laudanine only by the interchange in position of a hydroxyl and a methoxyl group. The *hydrochloride*, *platinichloride*, *chromate*, *picrate*, m. p. 162—163°, and *perchlorate* of the base are mentioned. C. S.

Syntheses of Dihydro*iso*quinoline Derivatives. HERMAN DECKER, WALTER KROPP, HEINRICH HOYER, and PAUL BECKER (*Annalen*, 1913, **395**, 299—320. Compare Pictet and Kay, A., 1909, i, 513 ; Decker and Kropp, *ibid.*, i, 513).—Derivatives of 3 : 4-dihydro-*iso*quinoline are obtained by the interaction of acyl-β-phenylethyl-amides and phosphorus pentachloride and phosphoryl chloride in boiling benzene, toluene, or xylene, moisture being carefully excluded. Formo-β-phenylethylamide yields very little 3 : 4-dihydro*iso*quinoline (*picrate*, m. p. 174—176°), the chief products being β-phenylethylamine and β-phenylethylaminomalon-β-phenylethylamide (Decker and Becker, A., 1911, i, 714). Phenylaceto-β-phenylethylamide, treated as in Decker and Kropp's method (*loc. cit.*), yields *di-β-phenylethylamine* (?), $NH(CH_2 \cdot CH_2Ph)_2$, b. p. 220—230°/30 mm. (*picrate*, m. p. 229—231°), and 1-benzyl-3 : 4-dihydro*iso*quinoline (picrate, m. p. 182°, not 174—175° [Pictet and Kay, *loc. cit.*]). Oxalodi-β-phenylethylamide yields a *substance* (*hydrochloride*, m. p. 191—193° ; *picrate*, $C_{24}H_{21}O_8N_5$, m. p. 167—168°, canary-green needles), which is probably 3 : 4-*dihydro*iso-*quinolyl*-1-*carboxy*-β-*phenylethylamide*, $C_9NH_8 \cdot CO \cdot NH \cdot CH_2 \cdot CH_2Ph$, since it yields β-phenylethylamine and a derivative of *iso*quinoline by hydrolysis by hydrochloric acid at 120°. Even by energetic treatment, the substance cannot be converted into bis-3 : 4-dihydro*iso*quinolyl.

Homopiperonoylhomopiperonylamine yields 1-*piperonylnorhydras-tinine* (annexed formula), m. p. 136—137°, colourless plates (*picrate*, m. p. 220—223° [decomp.] ; *platini-chloride*, decomp. 175—180°), to-gether with another base, *picrate*, m. p. 228°.

Phenylacetohomopiperonylamide yields 1 - benzylnorhydrastinine

(*picrate*, m. p. 205—206° [decomp.]), whilst *benzohomopiperonylamide*, $CH_2O_2:C_6H_3\cdot CH_2\cdot CH_2\cdot NH\cdot COPh$, m. p. 122°, colourless needles, prepared by heating *homopiperonylamine benzoate*, m. p. 115°, yellowish-green needles, at 180° (compare this vol., i, 272), or from homopiperonylamine by the Schotten-Baumann method, yields 1-*phenylnorhydrastinine*, $C_{16}H_{13}O_2N$, m. p. 141°, colourless prisms (*methiodide*, m. p. 241° ; *picrate*, m. p. 188—190°).

Formohomopiperonylamide yields by condensation *norhydrastinine*,

$$CH_2O_2:C_6H_2 \underset{CH=N}{\overset{CH_2\cdot CH_2}{<}},$$ m. p. 90—91°, stout needles (*picrate*, m. p.

237—238° ; *hydrochloride*, m. p. 192° ; *platinichloride*, decomp. about 240°), the chief product, however, being *homopiperonylaminomalondihomopiperonyldiamide*,

$$CH_2O_2:C_6H_3\cdot CH_2\cdot CH_2\cdot NH\cdot CH(CO\cdot NH\cdot CH_2\cdot CH_2\cdot C_6H_3\cdot CH_2O_2)_2,$$

m. p. 124—126° (decomp.), colourless needles, which forms a *picrate*, m. p. 210—211° (decomp.), yellow plates, and *hydrochloride*, m. p. 182—183°.   C. S.

Syntheses of Hydrastinine and its *N*-Homologues. HERMAN DECKER (*Annalen*, 1913, **395**, 321—328).—Norhydrastinine (preceding abstract) and methyl sulphate react in toluene at 100° to form 2-*methylnorhydrastinine methosulphate* (*hydrastinine methosulphate*),

$$C_{10}H_9O_2NMe\cdot SO_4Me,$$

m. p. 117—119°, pale yellow, crystalline powder, from which hydrastinine is liberated by 15% sodium hydroxide at 0°.

Norhydrastinine in alcohol reacts with benzyl chloride at 50° to form the *benzylochloride*, $C_{10}H_9O_2NCl\cdot CH_2Ph$, m. p. 215°, pale yellow powder, and with ethyl iodide to form the *ethiodide*, $C_{10}H_9O_2NEtI$, m. p. 222°, yellow leaflets ; 2-*ethylnorhydrastinine picrate* has m. p. 175°.   C. S.

Synthesis of Cotarnine and Third Synthesis of Hydrastinine. HERMAN DECKER and PAUL BECKER (*Annalen*, 1913, **395**, 328—342). —*Formylhomomyristicylamine*, $CH_2O_2:C_6H_2(OMe)\cdot CH_2\cdot CH_2\cdot NH\cdot CHO$, m. p. 105—106° (corr.), colourless needles, obtained by heating homomyristicylamine formate at 160—170° for three hours, is converted, by phosphoryl chloride in boiling toluene and subsequently basifying the aqueous solution of the product, into *norcotarnine*,

$$CH_2O_2:C_6H(OMe) \underset{CH=N}{\overset{CH_2\cdot CH_2}{<}},$$
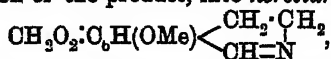
(*picrate*, m. p. 182—184°, yellow needles), the methiodide of which, m. p. 184—186° (decomp.), is identical with cotarnine hydriodide, and the methosulphate of which is converted into cotarnine picrate (Salway, T., 1911, **97**, 1208) by alcoholic picric acid.

Equal molecular quantities of homopiperonylamine and benzaldehyde react on the water-bath to form *benzylidenehomopiperonylamine*, $CH_2O_2:C_6H_3\cdot CH_2\cdot CH_2\cdot N:CHPh$, m. p. 36°, pale yellow prisms, which is converted by methyl iodide (without a solvent) at 100° into the *methiodide*. The latter is hydrolysed by boiling 95% alcohol or by steam, yielding benzaldehyde and *homopiperonylmethylamine hydriodide*,

m. p. 135—136° (corr.), colourless leaflets. *Homopiperonylmethylamine*, $C_{10}H_{13}O_3N$, b. p. 156—158°/24 mm., pale yellow oil (*carbonate*, m. p. 72—75°; *hydrochloride*, m. p. 183—185°; *picrate*, m. p. 166—167° [corr.]), is converted into formylhomopiperonylmethylamine by heating its formate at 150—160° for seven hours. By condensation with phosphoryl chloride in boiling toluene and basification of the product, the formyl derivative is converted into hydrastinine.

By processes similar to the preceding, *benzylidenehomopiperonylamine* and its *ethiodide*, homopiperonylethylamine hydriodide, m. p. 126—128°, white leaflets, and the corresponding *hydrochloride*, m. p. 183—185°, and *picrate*, m. p. 135—136°, orange-red leaflets, *formylhomopiperonylethylamine*, and 2-ethylnorhydrastinine (preceding abstract) have been prepared.

When a certain temperature or duration of heating is exceeded, by-products are obtained in the interaction of benzylidenehomopiperonylamine and an alkyl haloid. Their production is due to the formation of homopiperonyl haloid, which reacts with the benzylidene compound in the same manner as does the alkyl haloid, a derivative of dimethylamine being produced simultaneously. As an illustration of such heterospasis (compare Decker and Fellenberg, A., 1909, i, 116), equal molecular quantities of benzylidenehomopiperonylamine and methyl iodide have been heated in benzene at 140° for six hours and the product has been hydrolysed by steam, whereby *dihomopiperonylamine hydriodide*, $NH(CH_2 \cdot CH_2 \cdot C_6H_3 \cdot CH_2O_2)_2,HI$, m. p. 234—236°, pale yellow prisms, has been obtained. The corresponding *base* has m. p. 72—75° (decomp.).

Moreover, quaternary ammonium haloids are formed when moisture is present during the interaction of benzylidenehomopiperonylamine and an alkyl haloid; in the preceding example, *homopiperonyltrimethylammonium iodide*, m. p. 260—261°, is formed. C. S.

Syntheses of Tetrahydroisoquinoline Derivatives.

HERMAN DECKER and PAUL BECKER (*Annalen*, 1913, **395**, 342—362).—Homopiperonylamine or a similar derivative of β-phenylethylamine reacts readily at the ordinary temperature with an equal molecular quantity of an aldehyde to form the alkylidene derivative, which is converted into a tetrahydroisoquinoline derivative by a suitable catalyst; homopiperonylamine (or similar base) and the aldehyde, reacting directly in the presence of the catalyst, yield quite different products.

By adding slowly a benzene solution of benzylidenehomopiperonylamine to moderately warm, concentrated hydrochloric acid, the *hydrochloride*, m. p. 309—311°, of 1-*phenyldihydronorhydrastinine*,

$$CH_2O_2{:}C_6H_2\underset{\diagdown CHPh \cdot NH}{\overset{\diagup CH_2---CH_2}{\big<}},$$
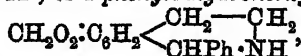
m. p. 97—98°, large, hexagonal leaflets, is obtained; the *nitrate* and *picrate*, m. p. 169—170° (decomp.), dark yellow prisms, are described. The same base is produced by reducing 1-phenylnorhydrastinine (preceding abstract) by alcohol and 2·5% sodium amalgam, the solution being kept acid by the addition of glacial acetic acid.

Piperonylidenehomopiperonylamine, m. p. 117—118° (unstable *picrate*, m. p. 143—145°), and *cinnamylidenehomopiperonylamine*, m. p.

61—63°, are respectively prepared from equal molecular quantities of the components on the water-bath.

The slow addition of homopiperonylamine to 20% formaldehyde yields *homopiperonylmethylenamine*, CH_2O_2:C_6H_3·CH_2·CH_2·N:CH_2, a liquid, which is converted by hydrochloric acid on the water-bath into the *hydrochloride*, m. p. 274—276°, of *dihydronorhydrastinine*, $C_{10}H_{11}O_2N$, m. p. 81—83°. This base, the hydrochloride of which is also obtained by reducing norhydrastinine with tin and hydrochloric acid, forms a *hydrobromide*, m. p. 256—258°, *picrate*, m. p. 229—231° (decomp.), and *carbonate*, m. p. 114—115° (decomp. corr.), and reacts in benzene with methyl iodide to form the hydriodide, m. p. 239—241° (Freund and Will record 232°) of dihydrohydrastinine. Dihydronorhydrastinine and methyl sulphate react in benzene to form a crystalline substance, m. p. 135—137°, which is converted, by successive treatment with sodium hydrogen carbonate and hydrochloric acid, into dihydrohydrastinine hydrochloride, m. p. 276—278°. Dihydrohydrastinine in the form of its hydrochloride is obtained directly from homopiperonylamine hydrochloride by heating it with 40% formaldehyde at 130° for three hours. The same hydrochloride is also produced from homopiperonylmethylamine hydrochloride or dihydronorhydrastinine hydrochloride and an excess of 40% formaldehyde at 120°.

The paper closes with an explanation of Eschweiler's process of methylation by means of formaldehyde which is represented by the scheme :

$$RR'NH,HX \longrightarrow RR'N \begin{cases} CH_2 \cdot OH \\ CH_2 \cdot OH \\ X \end{cases} \longrightarrow$$

$$RR'N \begin{cases} Me \\ CHO \\ X \end{cases} \longrightarrow RR'NMeX + H \cdot CO_2H.$$
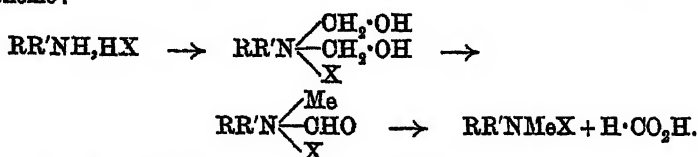
This explanation is in harmony with the fact that quaternary ammonium salts are not produced by Eschweiler's method, and, applied to phenols, will account for the frequent occurrence of the methoxyl group in plant substances.   C. S.

Synthesis of Pyrroles from Amino-ketones and Ketones or Ketonic Esters. OSCAR PILOTY and PAUL HIRSCH (*Annalen*, 1913, 395, 63—74).—The synthesis of pyrrole derivatives by Knorr's method of condensing amino-ketones and esters of β-ketonic acids in glacial acetic acid fails in many cases. The authors now find that condensation in alkaline solution is much more satisfactory, and that ketones can be used instead of ketonic esters. An aqueous solution of the amino-ketone hydrochloride is treated with an excess of an alkali hydroxide, the ketone or ketonic ester is added, and the closed vessel is kept at a gentle heat or left for several days at the ordinary temperature; thus aminoacetone yields 2 : 4-dimethylpyrrole with acetone, 2-*phenyl-4-methylpyrrole*, m. p. 152°, with acetophenone, 2 : 3 : 4-trimethylpyrrole with methyl ethyl ketone, 3 : 4-*dimethyl-2-ethylpyrrole*, an oil (*picrate*, m. p. 122·5°), with diethyl ketone, whilst methyl α aminoethyl ketone yields 2 : 3 : 5-*trimethylpyrrole*, b. p. 75·5—76·5°/16 mm. (and tetramethylpyrazine as a by-product), with

acetone, and $2:3:4:5$-*tetramethylpyrrole* (*picrate*, m. p. 125—126°), and chiefly tetramethylpyrazine, with methyl ethyl ketone.

Aminoacetone yields ethyl $2:4$-dimethylpyrrole-3-carboxylate with ethyl acetoacetate, and *ethyl hydrogen 3-methylpyrrole-4 : 5-dicarboxylate*,

$$NH \Big\langle {}^{CH=\!\!=\!\!=CMe}_{C(CO_2H)\cdot C\cdot CO_2Et},$$ m. p. 196°, with ethyl oxalacetate; by hydrolysis the ethyl hydrogen ester is converted into *3-methylpyrrole-4(or 5)-carboxylic acid*, m. p. 149°, which yields 3-methylpyrrole by heating.

Methyl α-aminoethyl ketone yields *ethyl hydrogen 2 : 3-dimethylpyrrole-4 : 5-dicarboxylate*, m. p. 201° (decomp.), and tetramethylpyrazine, with ethyl oxalacetate. By hydrolysis the ester yields $2:3$-*dimethylpyrrole-4(or 5)-carboxylic acid*, m. p. 188°, which decomposes at 190—195° in carbon dioxide to form $2:3$-*dimethylpyrrole*, b. p. 62°/11 mm. (*picrate*, $2C_6H_9N,C_6H_2(NO_2)_3\cdot OH$, m. p. 146·5°).

C. S.

A New Method of Preparing Cyclamine-aldehydes and -alcohols. II.

ADOLF KAUFMANN and LOUIS G. VALLETTE (*Ber.*, 1913, 46, 49—57. Compare A., 1912, i, 655).—In the earlier paper, the aldehydes obtained by the scission of the condensation products of nitrosodimethylaniline with 2-methylquinoline ethiodide and α-picoline methiodide were isolated only as phenylhydrazones; processes are now described for the separation of the aldehydes in a free state.

6-Methoxylepidine ethiodide, yellow or brown needles decomposing at 177—179°, gives in dilute aqueous solution a beautiful blue fluorescence; it condenses with nitrosodimethylaniline when heated in alcoholic solution, with the formation of the p-*dimethylaminoanil* of *6-methoxyquinoline-4-aldehyde ethiodide*, green columns, m. p. 214—215°, which gives blue solutions in alcohol and carmine-red in water; this substance dissolves in dilute hydrochloric acid, undergoing scission into p-aminodimethylaniline and *6-methoxyquinoline-4-aldehyde ethiodide*, the latter of which can be easily separated as the *phenylhydrazone*, red needles decomposing near 248°.

The dimethylaminoanil of quinoline-2-aldehyde ethiodide (*loc. cit.*) is hydrolysed by mineral acid, and phenylhydrazine precipitates the phenylhydrazone of quinoline-2-aldehyde ethiodide; if the addition of the phenylhydrazine be delayed for a time, the precipitate obtained is a mixture of the above with the *phenylhydrazone* of *quinoline-2-aldehyde ethochloride*, red needles, m. p. 180° (decomp.), which on reduction with zinc and dilute hydrochloric acid yields a pungent smelling, oily *base*, together with some aniline.

The hydrolysis of the dimethylaminoanil of pyridine-2-aldehyde methiodide likewise yields the methiodide and *methochloride* of the aldehyde, which can be separated as the phenylhydrazones, that of the methochloride decomposing near 235° after previous fusion in its water of crystallisation near 70°.

If the phenylhydrazone of pyridine-2-aldehyde methiodide, after previous careful removal of water of crystallisation, is heated below its m. p. (244°) under 0·1—0·2 mm. pressure (obtained by Wohl's

method with liquid air and charcoal), methyl iodide is liberated with the formation of *pyridine-2-aldehyde phenylhydrazone*, yellow needles or leaflets, m p. 180—182°; *hydrochloride*, orange-yellow needles, m. p. 188° (decomp.). The methochloride can also be used for the reaction.

In a similar manner the phenylhydrazone of quinoline-2-aldehyde ethiodide can be decomposed to produce *quinoline-2-aldehydephenylhydrazone*, yellowish-brown needles or leaflets, m. p. 203—204°; *hydrochloride*, red needles, m. p. about 237° (decomp.) (compare von Miller and Spady, A., 1886, 370).

Pyridine-2-aldehydephenylhydrazone undergoes reversible hydrolysis when treated with warm mineral acid, but the addition of dinitrobenzaldehyde causes the removal of the phenylhydrazine by forming a very sparingly soluble phenylhydrazone, and the hydrolysis then proceeds to completion ; free *pyridine-2-aldehyde* is a pungent liquid, b. p. 210°/725 mm., which gives the usual aldehyde reactions except with Fehling's solution.

Quinoline-2-aldehyde, obtained by hydrolysis of the phenylhydrazone at 120—130° under pressure, forms colourless tablets, m. p. 70—71° (compare von Miller and Spady, *loc. cit.*).   D. F. T.

4-Quinolyl Ketones. II. ADOLF KAUFMANN, MAX KUNKLER, and HEINRICH PEYER (*Ber.*, 1913, **46**, 57—64. Compare A., 1912, i, 1017).—From a comparison of the cinchona alkaloids the conclusion is drawn that a substance of the structure 6-alkyloxy-4-(β-dialkylamino-a-hydroxyalkyl)-quinoline should possess properties similar to those of quinine.

4-Quinolyl methyl ketone has b. p. 99°/0·08 mm., and 4-quinolyl phenyl ketone, m. p. 59°, b. p. 142°/0·12 mm.

6-Ethoxyquinoline (Kaufmann and Peyer, A., 1912, i, 650) readily unites with methyl sulphate with the formation of a yellow solid, the fluorescent solution of which when treated with potassium cyanide yields *4-cyano-6-ethoxy-1-methyl-1 : 4-dihydroquinoline* ; the ethereal extract of this substance is oxidised by alcoholic iodine to red needles of *4-cyano-6-ethoxyquinoline methiodide*, m. p. 183—184° (decomp.), which when heated near its m. p. in a vacuum liberates methyl iodide, leaving free *4-cyano-6-ethoxyquinoline* as yellow needles m. p. 118°, which give fluorescent solutions. When treated in benzene solution with an ethereal solution of magnesium methyl iodide the cyano-compound is converted into 6-*ethoxy-4-quinolyl methyl ketone*, golden-yellow leaflets or needles, m. p. 80—81°, whilst with magnesium ethyl iodide in an analogous manner, 6-*ethoxyquinolyl ethyl ketone*, golden-yellow crystals, m. p. 92°, is produced ; both ketones with dilute acids give yellow solutions with a greenish fluorescence.

6-Methoxy-4-quinolyl methyl ketone, dissolved in acetic acid of 50% concentration, is reduced by zinc dust to 6-*methoxy-4-quinolyl methyl carbinol*, needles, m. p. 120—121°, which gives a blue fluorescence in dilute sulphuric acid, and an emerald-green coloration with chlorine water and ammonia.

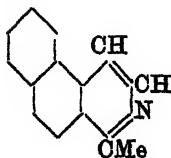4-Quinolyl methyl ketone in alcoholic solution containing sodium

ethoxide is converted by amyl nitrite into 4-*quinolyl oximinomethyl ketone*, colourless needles, m. p. 237—242° (decomp.), which gives a yellow *substance* with phenylhydrazine, and is reduced by an acid solution of stannous chloride to β-*amino-α-hydroxy-4-quinolylethane* (annexed formula); *hydrochloride*, a greyish-white powder, m. p. 208—210° (decomp.); *picrate*, leaflets, m. p. 202°.

$CH(OH)\cdot CH_2\cdot NH_2$
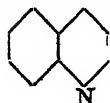
D. F. T.

A Methylnaphthaisoquinoline. Amé Pictet and B. Manevitch (*Arch. Sci. phys. nat.*, 1913, [iv], **35**, 40—47. Compare Pictet and Gams, A., 1909, i, 671).—The preparation of 1-methyl-α-naphthaisoquinoline (annexed formula) is described.

A mixture of α- and β-naphthyl methyl ketones was obtained by the addition of aluminium chloride to a solution of naphthalene and acetyl chloride in carbon disulphide. The two isomerides were separated by treatment of their alcoholic solution with a saturated solution of picric acid, whereby the α-naphthyl methyl ketone picrate was precipitated, from which, by decomposition with sodium carbonate, α-naphthyl methyl ketone, b. p. 292—293°, was isolated in 25—30% yield. β-Naphthyl methyl ketone, b. p. 171—172°/12 mm., m. p. 51°, was obtained from the mother liquor, the yield being 12—15%. Attempts to prepare the α-ketone by the action of acetyl chloride on an ethereal solution of magnesium α-naphthyl bromide were less successful.

α-*Naphthyl oximinomethyl ketone*, m. p. 183°, was formed by the gradual addition of amyl nitrite to an alcoholic solution of α-naphthyl methyl ketone in the presence of sodium ethoxide, and was transformed into α-*naphthyl aminomethyl ketone hydrochloride*, m. p. 245—250° (decomp.) by reduction with stannous chloride. The free *base* was unstable.
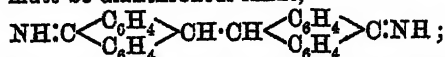
α-*Naphthyl acetylaminomethyl ketone*, $C_{10}H_7\cdot CO\cdot CH_2\cdot NHAc$, m. p. 103°, prepared by the action of acetic anhydride and potassium hydroxide on a concentrated aqueous solution of the above hydrochloride, was reduced by means of sodium amalgam to the corresponding *carbinol*, needles, m. p. 145—146°, which, when treated with phosphoric oxide in boiling xylene solution, was transformed into 1-*methyl-α-naphthaisoquinoline*, m. p. 95—96°.

H. W.

Amino-Imino-Desmotropy. Kurt H. Meyer and Hans Schlosser (*Ber.*, 1913, **46**, 29—32).—It has already been shown (Meyer, A., 1911, i, 193) that 9-hydroxyanthracene exhibits tautomerism between its enolic and ketonic isomeric structures (anthranol and anthrone), and it is now discovered that similar tautomerism can exist in the anthracene group with 9-aminoanthracene derivatives.

The oxidation of 9-aminoanthracene by amyl nitrite (Kaufler and Suchannek, A., 1907, i, 225) or by bromine in alcoholic solution gives

rise to a substance, m. p. 204—205°, which from its lack of colour and of fluorescence must be dianthronedi-imine,

$$\mathrm{NH{:}C}\!\!\begin{array}{c}\mathrm{C_6H_4}\\\mathrm{C_6H_4}\end{array}\!\!\!\!>\!\!\mathrm{CH\cdot CH}\!\!<\!\!\begin{array}{c}\mathrm{C_6H_4}\\\mathrm{C_6H_4}\end{array}\!\!\!\!\mathrm{C{:}NH} \; ;$$

it is a diacid base, and the course of the oxidation is evidently analogous to that of anthranol (Meyer, *loc. cit.*). When the substance is boiled for an hour with a methyl-alcoholic solution of potassium hydroxide, it is converted into the isomeric diaminodianthryl,

$$\mathrm{NH_2\cdot C}\!\!<\!\!\begin{array}{c}\mathrm{C_6H_4}\\\mathrm{C_6H_4}\end{array}\!\!\!\!>\!\!\mathrm{C\cdot C}\!\!<\!\!\begin{array}{c}\mathrm{C_6H_4}\\\mathrm{C_6H_4}\end{array}\!\!\!\!>\!\!\mathrm{C\cdot NH_2},$$
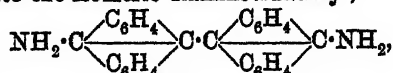
golden-yellow leaflets, m. p. 334° (compare Gimbel, A., 1887, 1049), which dissolves in benzene to a solution with a green fluorescence. The same isomeric change can be induced less readily by boiling with acetic acid or by fusion, but the reverse change from the amino- to imino-compound could not be accomplished. **D. F. T.**

Phenylbenzylidenehydrazine. GEORG LOCKEMANN and FRANZ LUCIUS (*Ber.*, 1913, **46**, 150—152).—Thiele and Pickard (A., 1898, i, 474) obtained by the action of acetic anhydride and zinc chloride or sulphuric acid on phenylbenzylidenehydrazine an isomeric β-modification of the hydrazine, m. p. 136°. On repetition the only product now obtained is α-acetyl-α-phenyl-β-benzylidenehydrazine, m. p. 122°. **E. F. A.**

Constitution of "Anilipyrine." EZIO COMANDUCCI (*Boll. chim. farm.*, 1912, **51**, 741—743).—Two "anilipyrines" have been described, of which one was supposed to result from the condensation of equimolecular quantities of antipyrine and acetanilide, and the other from two molecules of antipyrine with one molecule of acetanilide. By the method of thermal analysis, the author now shows that these substances are neither compounds nor even mixed crystals, but consist simply of crystalline mixtures. When fused mixtures of the antipyrine and acetanilide are cooled, an eutectic is observed corresponding with 45% of antipyrine and 45°. The behaviour of the "anilipyrines" with solvents supports the above results. **R. V. S.**

Constitution of "Anilipyrine." LINO METELLO ZAMPOLLI (*Boll. chim. farm.*, 1912, **51**, 780—782. Compare preceding abstract).—Polemical. The author appears to be in agreement with Comanducci's conclusions as now stated. From his preliminary experiments, however, the eutectic temperature is at least 48·5°. **R. V. S.**

Reaction Products from 1-Phenyl-3-methyl-5-pyrazolone and Phthalic Anhydride. GUSTAV SCHULTZ and GEORG ROHDE (*J. pr. Chem.*, 1913, [ii], **87**, 119—142.)—When crystallised from ethyl acetate or acetone, the product, formed by fusing 1-phenyl-3-methyl-5-pyrazolone with phthalic anhydride in equimolecular proportions at 120°, yields an orange-yellow, crystalline *substance*, which becomes red and melts at 202—204°, and on crystallisation from methyl alcohol and acetic acid, or on treatment with aqueous alkalis, loses phthalic

acid and is converted into the red substance first observed by Knorr (A., 1887, 601).

The latter compound is best prepared by boiling the product of the fusion with water until it is completely soluble in chloroform. It crystallises in clusters of dark red prisms or thin, lancet-shaped leaflets, m. p. 208—210° or above, according to the rapidity of heating, and when heated with phthalic acid in acetone or ethyl acetate solution is transformed into the above-mentioned yellow substance.

The constitution of the red substance is represented by one of the following formulæ :

$$C \cdot C_6H_4 \cdot CO_2H \qquad\qquad C \cdot C_6H_4 \cdot CO_2H$$

$$N{<}{\overset{CMe \cdot C}{NPh \cdot CO}}{\overset{CH \cdot CMe}{CO-NPh}}{>}N \qquad N{<}{\overset{CMe \cdot C}{NPh \cdot CO}}{\overset{C \text{---} CMe}{C(OH) \cdot NPh}}{>}N.$$

It separates from methyl alcohol and chloroform in red prisms, containing the solvent, and dissolves in aqueous alkalis and alkaline carbonates, forming orange-red salts ; the red mono- and di-*silver* salts are mentioned. With methyl-alcoholic hydrogen chloride, it forms a *methyl* ester, $C_{29}H_{24}O_4N_2$, which crystallises in orange-yellow prisms or plates having a bluish glance, m. p. 178—179°, and yields a red *silver* salt, $C_{29}H_{23}O_4N_4Ag$. When heated in nitrobenzene solution or in other solvents of high b. p., the red substance decomposes into 1-phenyl-3-methyl-5-pyrazolone and 1-*phenyl-3-methyl-4-pyrazol-5-onyl-idenephthalide*, $\overset{N=CMe}{\underset{NPh \cdot CO}{|}}{>}C{:}C{<}\overset{C_6H_4}{\underset{O}{|}}{>}CO$. This crystallises in slender, red needles, which sinter at 208°, and have m. p. 212—219°, according to the rapidity of heating. It combines with 1-phenyl-3-methyl-5-pyrazolone in boiling cumene solution to form the original red compound, and is resolved by aqueous alkalis into the ketonic *acid*, $\overset{N=CMe}{\underset{NPh \cdot CO}{|}}{>}CH \cdot CO \cdot C_6H_4 \cdot CO_2H$, which forms lustrous, yellow leaflets of variable m. p. (145—160°), and is reconverted by the action of acetic anhydride into the phthalide.

When warmed with acetic anhydride and a little sulphuric acid, the original red substance is transformed into an *anhydride* (annexed formula), crystallising in slender, colourless needles, m. p. 261°; the reverse transformation may be effected by boiling the anhydride with alcoholic alkali hydroxides.

$$C_6H_4{<}{\overset{CO}{C}}{>}O$$

$$N{<}{\overset{CMe \cdot C}{NPh \cdot C}}{\underset{O}{-}}{\overset{C \cdot CMe}{C \cdot NPh}}{>}N$$

F. B.
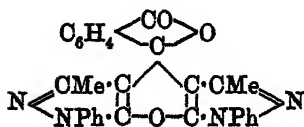
The Constitution of the Pyrazolinecarboxylic Acids. AUGUST DARAPSKY (*Ber.*, 1913, **46**, 218—225).—Polemical ; a reply to Bülow (this vol., i, 101).

D. F. T.

A New Example of the Reversed Pinacolin Rearrangement. HEINRICH BILTZ and KARL SEYDEL (*Ber.*, 1913, **46**, 138—142).—4:5-Di-phenyldihydroglyoxalone, $\overset{CPh \cdot NH}{\underset{CPh \cdot NH}{|}}{>}CO$, is oxidised by nitric acid to

4:5-diphenyldihydroglyoxalone glycol, $\begin{array}{c}\text{HO·CPh·NH}\\\text{HO·CPh·NH}\end{array}{>}\text{CO}$, which in presence of alkaline hydroxides undergoes a normal pinacolin rearrangement into 5:5-diphenylhydantoin, $\begin{array}{c}\text{CPh}_2\text{·NH}\\\text{CO——NH}\end{array}{>}\text{CO}$ (compare Biltz, A., 1909, i. 525).

When this hydantoin is energetically reduced with hydrogen iodide and phosphorus, 4:5-diphenyldihydroglyoxalone is obtained together with decomposition products, the phenyl group returning to its original place.

The decomposition products include diphenylacetic acid and diphenylmethane, indicating that in the hydantoin the two phenyl residues are attached to the same carbon atom.

On reducing 5:5-diphenylhydantoin by distillation with zinc dust, diphenylmethane and benzonitrile are formed, the latter being due to the rearrangement into diphenylglyoxalone which gives rise to benzonitrile when distilled with zinc dust.

Di-p-bromo-4:5-diphenylhydantoin is very resistant to hydrogen iodide and phosphorus. Only bis-p-bromophenylmethane could be isolated from the reaction products; the presence of di-p-bromodiphenylacetic acid and of di-p-bromodiphenyldihydroglyoxalone was made probable.   E. F. A.

Phenazine. FRIEDRICH KEHRMANN and EM. HAVAS (*Ber.*, 1913, **46**, 341—352).—The authors have obtained good yields of phenazine by the action of *o*-aminodiphenylamine on *o*-nitrodiphenylamine in the presence of anhydrous sodium acetate, and have examined several of its derivatives.

o-Nitrodiphenylamine was obtained in 85—90% yield by heating *o*-chloronitrobenzene, aniline, and anhydrous sodium acetate during twelve to fifteen hours at 215°. Reduction of its alcoholic solution by stannous chloride and hydrochloric acid gave *o*-aminodiphenylamine. For the preparation of phenazine, *o*-nitrodiphenylamine, *o*-aminodiphenylamine, and anhydrous sodium acetate were heated at about 250°, when a violent reaction occurred. The phenazine was isolated by distillation of the crude product, or, better, by treatment with superheated steam; yield, 60—70%. In the absence of sodium acetate, only traces of phenazine could be obtained.

When dissolved in nitrobenzene and treated with methyl sulphate, phenazine yielded *methylphenazonium methosulphate* as greenish-yellow prisms. The corresponding *platinichloride*, $C_{26}H_{22}N_4Cl_6Pt$, and *dichromate*, $C_{26}H_{22}N_4O_7Cr_2$, were analysed, but the *chloride*, *bromide*, and *nitrate* were found to be so readily soluble in water that they could not be precipitated from a solution of the sulphate. When concentrated aqueous potassium iodide was added to an aqueous solution of methylphenazonium methosulphate, an orange-coloured solution was obtained, which, after a short time, deposited greenish-black needles. The latter dissolved readily in hot alcohol with formation of a greenish-yellow solution, which, when rapidly cooled, yielded bluish leaflets, which could be ground to a dirty-green powder.

Analyses of the crystals yielded figures agreeing with those required by the normal iodide, $C_{13}H_{11}N_2I$. The authors, however, are led to the conclusion that this substance is only contained in the yellow solution, and that the crystals probably consist of a quinhydrone salt composed of 1 mol. of methylphenazonium tri-iodide and 2 mols. of methyldihydrophenazine.

In the presence of air, sodium hydroxide transformed a solution of methylphenazonium methosulphate into phenazine mixed with small quantities of a red *substance*, probably having the annexed formula. Similarly, aqueous ammonia yielded mainly phenazine when brought into reaction with methylphenazonium salts, but, in the absence of water, salts of 3 aminomethylphenazonium were readily obtained. Of these, the following were isolated, namely, the *chloride*, *bromide*, and *nitrate*, green needles which yielded magenta-red solutions, and the *platinichloride*.

1 : 3-*Dinitrophenazine* was obtained by cautiously heating phenazine with sulphuric acid and rather more than the calculated amount of nitric acid to 130°. It crystallised in yellow needles, which had no definite m. p., but decomposed above 200°. Reduction of this substance by hydrogen sulphide in ammoniacal alcoholic solution led to the formation of dinitrodihydrophenazine (annexed formula), the constitution of which follows from its identity with the compound prepared by Kehrmann and Messinger (A., 1894, i, 55), and by Leemann and Grandmougin (A., 1908, i, 478), from o-phenylenediamine and picryl chloride. Attempts to reduce 1 : 3-dinitrophenazine or its dihydro-derivative to diaminophenazine were unsuccessful.

The authors have re-investigated the acetylation of dihydrophenazine (compare Hinsberg and Garfunkel, A., 1897, i, 123; Tichwinski and Wolochowitsch, A., 1905, i, 383; Hinsberg, A., 1905, i, 840). They find that pure acetic anhydride and pure dihydrophenazine yield only a monoacetyl derivative, whilst the diacetyl derivative is immediately formed if a trace of zinc chloride is added. They consider that dihydrophenazine and its diacetyl derivative possess a symmetrical structure, whilst the yellow monoacetyl derivative and dihydrophenazine sulphate are probably derived from the annexed unsymmetrical form.

A solution of dihydrophenazine diacetate in glacial acetic acid was mixed with concentrated nitric acid and warmed on the water-bath, whereby a mixture of 2-*nitrophenazine*, m. p. 214°, and *nitrodiacetyldihydrophenazine*, m. p. 166°, was obtained. The latter substance yielded 3-aminophenazine when warmed with concentrated sulphuric acid.

2-Aminophenazine (compare Fischer and Hepp, A., 1889, 500) was obtained by reduction of an alcoholic solution of nitrodiacetyldihydrophenazine by stannous chloride and hydrochloric acid, oxidation of the tin salt so obtained by ferric chloride solution, and liberation of the base by means of ammonia. H. W.
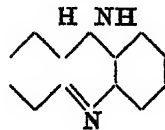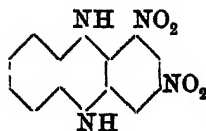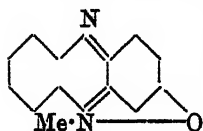
New Methods of Preparation of Asymmetric $\alpha\beta$-Naphthazine. Fritz Reitzenstein and Franz Andre (*J. pr. Chem.*, 1913, [ii], **87**, 97—118).—*as*-$\alpha\beta$-Naphthazine (Fischer and Junk, A., 1893, i, 283) has been prepared (1) from β-naphthylamine by the action of sulphur monochloride or sulphuryl chloride in pyridine solution, and also by distillation over magnesium and barium peroxides; (ii) from α-naphthylamine by heating with calcium oxide, and (iii) by sublimation of aceto-β-naphthylamide over a mixture of barium peroxide and calcium oxide. It forms greenish-yellow crystals, m. p. 278—281°, according to the method of preparation, and yields a dinitro-derivative, m. p. 330—332°, which is reduced by aqueous sodium sulphide to diaminonaphthazine (compare D.R.-P. 166363). When warmed with alcohol and hydrochloric acid, it forms an unstable red *hydrochloride*.

In pyridine solution, sulphuryl chloride reacts with α-naphthylamine, yielding a red *substance*, m. p. 169°, and with aceto-β-naphthylamide to form aceto-1-chloro-β-naphthylamide.

When distilled over a mixture of barium peroxide and calcium oxide, benzidine yields a substance, m. p. 122°, probably identical with the azine, $NH_2 \cdot C_6H_4 \cdot C_6H_3 < \!\!\!\begin{smallmatrix} N \\ N \end{smallmatrix}\!\!\!> C_6H_3 \cdot C_6H_4 \cdot NH_2$, isolated by Kalb (*Diss.*, München, 1905) from the product obtained by oxidising benzidine. The action of sulphuryl chloride on benzidine in pyridine solution gives rise to a *substance*, m. p. 126°, which is considered to be a chloroderivative of benzidine or of the above-mentioned azine.   F. B.

Synthesis of Two Isomeric Oxytetrazoles from Azoimide and Fulminic Acid. F. Carlo Palazzo and G. Marogna (*Gazzetta*, 1913, **43**, i, 69—80).—The interaction of azoimide and fulminic acid yields, not only the 1-hydroxytetrazole previously described (compare Palazzo, A., 1910, i, 342), but also an isomeride of this substance. Its formation is favoured by a low temperature. The *sodium* salt of iso*oxytetrazole*, $CHON_4Na,3H_2O$, forms large crystals, which have been described by Rosati (this vol., i, 207). It yields other salts by double decomposition, and gives also a *benzoyl* derivative, which crystallises in needles, m. p. 94°. The sodium salt is stable towards water and alkalis, but with sulphuric acid or with fuming hydrochloric acid suffers a decomposition analogous to that of its isomeride. The iso*oxytetrazole*, $CHON_3 \colon NH$, is obtained by treating the sodium salt with cold, dilute sulphuric acid; it has m. p. 155° (softening a few degrees previously). The decomposition of this substance with sulphuric acid is similar to that of the isomeride, but hydrochloric acid acts somewhat differently. The acid and its salts explode on percussion and also when heated.

The 1-hydroxytetrazole previously described forms when treated with diazomethane an ether containing a methoxyl group; it has m. p. 93—94°. The *iso*oxytetrazole forms an *N*-ether.

The authors consider that the *iso*oxytetrazole probably has the following structure: $\begin{smallmatrix} CH \colon NO \\ N =\!\!= N \end{smallmatrix}\!\!> NH$. They regard the production of these two isomerides from fulminic acid as a further proof of the tautomeric nature of that substance.   R. V. S.

Halogen Substitution Products of Azo-dyes. S. WEBER (*Monatsh.*, 1913, **34**, 243—254).—The influence of halogen substitution on the shade and usefulness of some dyes has been systematically studied.

Group A.— o-, m- and p-Chloro-, bromo-, and iodo-anilines, diazotised and coupled with β-naphthol-8-sulphonic acid in sodium carbonate solution, give yellow to red dyes, the p-compounds being darker and the m-compounds lighter than the o-members, whilst the shades deepen from chlorine to iodine.

Group B.—The same bases give redder dyes with α-naphthol-2 : 8-disulphonic acid, but the same generalisations may be made.

Group C.—Aniline, m- and p-bromoaniline do not couple so readily with 1-amino-β-naphthol-6-sulphonic acid, and the dyes are dark red tinged with blue.

Group D.—2 : 4-Dibromoaniline is less easily diazotised and coupled than the mono-derivatives, but gives deeper colours with the above sulphonates.

The dyes are faster than the unsubstituted analogues, and their colouring power is much enhanced. The ortho- and para-compounds are more valuable than the meta-, and the bromo- and iodo-derivatives are much more effective that the chloro-dyes.　　　　　J. C. W.

Congo-Red. I. Experimental Part. F. I. BOGOJAVLENSKI. II. Theoretical Part. VLADIMIR G. SCHAPOSCHNIKOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1813—1844).—The action of either strong or weak acids (even carbonic acid) on Congo-red results in the replacement of the sodium by hydrogen. With strong acids the action proceeds rapidly and yields a dark blue precipitate, which when washed gives a blue colloidal solution; the latter cannot be freed from admixed impurities by washing or dialysis. This solution of Congo-blue exhibits electrical conductivity, which is, however, probably conditioned by the impurities present. The action of weak acids gives the same product, but in a crystalline condition. Very small crystals of Congo-blue are capable of forming suspensions which closely resemble the colloidal solutions; both the colloidal particles and the crystals carry negative charges, both are coagulated without change of structure by acids or acid salts, and both the colloidal solution and the filtered crystalloidal suspension show Brownian movement under the ultramicroscope, the crystals passing through the filter.

The theoretical considerations of Part II lead to the following conclusions. The change in colour of substantive bisazo-colouring matters is conditioned by change in their intramolecular structure. The red forms of amino- and hydroxybisazo-colouring matters of the Congo-red type correspond with the azoid configuration of the molecules, whilst the blue forms correspond with the quinonoid structure. The instability of these forms and their ready interconversion are regarded as due to the agency of so-called "suspensive" linkings and of mobile hydrogen.　　　.　　T. H. P.

Aniline-Black and Allied Compounds. III. ARTHUR G. GREEN and SALOMON WOLFF (*Ber.*, 1913, 46, 33—49).—See P., 1912, 28, 250.

The Density and Solution Volume of Some Proteins. (Miss) HARRIETTE CHICK and CHARLES J. MARTIN (*Biochem. J.*, 1913, 7, 92—96).—A comparison was instituted in the case of four proteins, caseinogen, egg-albumin, serum-albumin, and serum-globulin, between the density directly determined with dry specimens and that calculated from the specific gravity of concentrated solutions. The latter is found to be 5 to 8% in excess of the former, showing the extent of shrinkage in volume taking place when these proteins enter into colloidal solution.   W. D. H.

The Hydrolysis of Organic Phosphorus Compounds by Dilute Acid and Dilute Alkali. R. H. ADERS PLIMMER (*Biochem. J.*, 1913, 7, 72—80).—Ethyl dihydrogen phosphate, glycerophosphoric acid, and phytic acid are hydrolysed by acid, but are stable to alkali. Hexose-phosphoric acid and phospho-protein behave so differently to alkali from the other three compounds mentioned, that they are probably not esters. In phospho-proteins, the phosphoric acid is probably united to one of the amino-acids. Hexose-phosphoric acid reduces Fehling's solution, which points to the presence of a functioning aldehyde or ketone group. Some suggestions as to atomic grouping are made to explain the differences in reaction referred to.
                                    W. D. H.

Protein Compounds. WALTER H. EDDY (*Biochem. Bull.*, 1912, 2, 111—122).—A description is given of protein salts formed by combining organic bases (strychnine, morphine, etc.) with acid reacting proteins (mucoids, nucleoproteins) and by combining the latter with basic reacting proteins, such as histone. It is pointed out that so-called histone, however, is itself probably a protein salt.
                                    W. D. H.

Bilirubin and Hæmin. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1913, 83, 170).—Polemical. A reply to Küster (this vol., i, 210).
                                    E. F. A.

The Action of Pepsin-Hydrochloric Acid on Proteins Partly Digested with Trypsin. VALDEMAR HENRIQUES and J. K. GJALDBÆK (*Zeitsch. physiol. Chem.*, 1913, 83, 83—92).—Egg-white and caseinogen partly digested with trypsin behave differently when submitted to the subsequent action of pepsin-hydrochloric acid, the former being more readily changed, and the yield of formaldehyde-titratable nitrogen being greater.   W. D. H.

Activity of Koji Sucrase [Invertase] in the Presence of Different Acids. GABRIEL BERTRAND, M. ROSENBLATT, and (Mme.) M. ROSENBLATT (*Compt. rend.*, 1913, 156, 261—263. Compare A., 1912, i, 148, 327, 401).—A study of the diastatic activity of the

sucrase, known as "taka-diastase," extracted from the Japanese Koji, in the presence of various acids. This sucrase, unlike those obtained from yeast and *Aspergillus niger*, shows a maximum activity in solutions the concentration of which with respect to hydrogen ions practically corresponds with neutrality to helianthin, and is independent of the nature of the acid. W. G.

Enzymic Decomposition of Glucosides and Galactosides. HENRY BIERRY (*Compt. rend.*, 1913, 156, 265—267. Compare A., 1909, ii, 747).—A résumé of the work already published on the enzymic hydrolysis of α- and β-glucosides and galactosides by various ferments. The author finds that the digestive juice of the *Helix* attacks both α- and β-galactosides. The lactase obtained from the intestine of a dog appears to be much more specific in its action, only attacking derivatives of galactose, and of these only the β-derivatives, from which it seems to make a restricted choice in that it hydrolyses lactose itself, but neither α- or β-methyl galactoside. W. G.

The Rate of Destruction of Ptyalin by the Direct Electric Current. W. E. BURGE (*Amer. J. Physiol.*, 1913, 31, 328—333).— The passage of the direct electric current destroys ptyalin, but this is not due to electrolytic products. The rate of destruction is uniform, and was 2·5% per coulomb for the solutions used. W. D. H.

Resistance of Emulsin to the Action of Heat in Presence of Strong Alcohol. EMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], 7, 65—67).—In a previous paper (this vol., i, 212), it was shown that the temperature at which emulsin is rendered inactive falls as the concentration of alcohol increases to 50%, but that with stronger alcohols the temperature of inhibition rises with the concentration of the alcohol. It was suggested that this phenomenon is due to the fact that in the stronger alcohols the ferment is precipitated, and in this condition is more resistant to heat. Experiments are now described which prove this contention ; thus, it was found that emulsin was scarcely weakened in action when mixed with dry alcohol, and the latter heated slowly to the boiling point and maintained at this temperature during two minutes. In sterilising plants containing enzymes, therefore, it is best to use alcohol of such a strength as to produce a liquid containing about 60% of alcohol when the plants are immersed in it, allowance being made for the water in the plants. T. A. H.

Enzyme Action. III. Action of Manganous Sulphate on Castor Bean Lipase. K. GEORGE FALK and MARSTON L. HAMLIN (*J. Amer. Chem. Soc.*, 1913, 35, 210—219. Compare Falk and Nelson, A., 1912, i, 523, 593).—Experiments are described which show that when a preparation of castor bean lipase which has been rendered inactive by heating with water is treated with manganous sulphate it becomes slightly active again. In order to explain this behaviour, it is suggested, that although the active enzyme is hydrolysed by the action of hot water, the inactive zymogen present in the pre-

paration is not wholly destroyed, and that the manganous sulphate effects the conversion of the inactive zymogen into active enzyme by a process of oxidation.   E. G.

Enzymic Decomposition of Hydrogen Peroxide. IV. PERCY WAENTIG and OTTO STECHE (*Zeitsch. physiol. Chem.*, 1913, **83**, 315—337. Compare A., 1911, i, 759 ; 1912, i, 228 ; ii, 839).—The action of several proteoclastic and other enzymes on active preparations of catalase has been studied. Trypsin alone destroys the catalase, indicating the protein nature of this substance. The experiments are not in favour of the possible destruction of a protective colloid by the trypsin, thereby destroying the catalase as well. The resistance of catalase to hydrolysis by pepsin suggests that it has a polypeptide structure, but it is possible that the experimental conditions were adverse to the action of pepsin, since the solutions could not be made more than faintly acid.

The gastric juice of the cray fish was especially active in destroying catalase—this confirms its tryptic nature. The action on catalase affords a method of detecting and possibly of measuring tryptic enzymes. Differences are noted in the resistance of blood catalase to the tryptic ferments of vertebrates and of the crayfish, and also in the behaviour of catalases of different origin to the same trypsin.

                                                    E. F. A.

Neutralisation of Solutions of Diaminodihydroxyarseno-benzene Hydrochloride. J. CHARLES BONGRAND (*J. Pharm. Chim.*, 1913, [vii], **7**, 49—55).—Theoretically this drug requires 4 mols. of sodium hydroxide to neutralise it by conversion into the disodium derivative. The author shows by means of cryoscopic and electrical conductivity determinations that in dilute solutions, as used in practice, hydrolytic dissociation occurs, and that more than the theoretical amount of sodium hydroxide is then required to maintain the drug in solution, as the disodium derivative.   T. A. H.

Phenylstibines. PAUL CARRÉ (*Bull. Soc. chim.*, 1913, [iv], **13**, 102—104).—Magnesium phenyl bromide reacts with antimony trichloride to form triphenylstibine together with the chlorides of phenyl stibine and diphenylstibine, the first being almost the sole product when a small proportion of the magnesium compound is used, whilst with 1 or 2 mols. larger quantities of the two latter substances are simultaneously produced. Phenylstibine and diphenylstibine chlorides are decomposed by heat into antimony trichloride and triphenylstibine (compare Michaelis and Günther, A., 1911, i, 1056).   T. A. H.

Mercury Dibenzyl. PAUL WOLFF (*Ber.*, 1913, **46**, 64—66).—The description of mercury dibenzyl given by Campisi, in 1865, is erroneous, and endeavours to prepare this substance by the action of sodium amalgam on benzyl chloride have been futile, producing only dibenzyl. The substance has been successfully obtained by the application of magnesium benzyl chloride [see Pope, following abstract].

Mercury dibenzyl is formed, and crystallises in long, colourless needles, m p. 111° [Pope and Gibson give 104°], which decompose above the m. p. into mercury and dibenzyl. When heated in alcoholic solution with mercuric chloride, *mercury benzyl chloride*, leaflets, m. p. 104°, is obtained ; *mercury benzyl bromide* and *mercury benzyl iodide*, prepared in an analogous manner, also form colourless leaflets, m. p. 119° and 117° respectively; *mercury benzyl cyanide*, needles, m. p. 124°, for its formation requires mercury dibenzyl and mercuric cyanide to be heated together in alcoholic solution at 130°. *Mercury benzyl acetate* is produced by the interaction of mercury dibenzyl and mercuric acetate in alcoholic solution, and also of mercury benzyl chloride and silver acetate in alcoholic solution.

Mercury dibenzyl when heated with acetic acid for two or three hours at 170° undergoes decomposition into mercury, toluene, benzyl acetate, and dibenzyl.   D. F. T.

Mercury Dibenzyl. WILLIAM J. POPE (*Ber.*, 1913, **46**, 352).— Mercury dibenzyl has been obtained previously to Wolff (preceding abstract) by Pope and Gibson, using the same method (T., 1912, **101**, 735).   T. S. P.

Physiological Chemistry.

The Effects of Muscular Exercise in Man. FRANK COOK and MARCUS S. PEMBREY (*J. Physiol*, 1913, **45**, 429—446).—The average composition of alveolar air in healthy men is oxygen, 14·9%, and carbon dioxide, 5·57%. The mean respiratory quotient was 0·9. Directly after muscular exercise the alveolar air contained 14·33% oxygen and 6·52% carbon dioxide; the mean respiratory quotient was 1. During muscular dyspnœa the respiratory quotient affords no definite indication of the metabolism, for the vigorous ventilation of the lungs washes out the carbon dioxide. The administration of oxygen is of value only in pathological conditions. The pulse rate in healthy men at rest varies from 45 to 90 per minute. In a trained man the pulse rate is slower during rest, has a wider range in response to muscular work, and rapidly recovers after exercise. "Second wind" is an adjustment of the respiratory and circulatory systems to the demands of the muscles for an adequate supply of blood; carbon dioxide is the chief factor in effecting the accommodation.   W. D. H.

Influence of Calcium and Potassium in the Respiratory Rhythm in Frogs. DONALD R. HOOKER (*Proc. Amer. physiol. Soc.*, 1912 ; *Amer. J. Physiol.*, **31**, xvii—xviii).—In the absence of calcium from a perfusion fluid, the respiratory centre is excited; in the absence of potassium it is depressed. In the presence of potassium decrease in the calcium causes depression, and an increase excita-

tion. In the presence of calcium, a decrease in the potassium causes excitation, and an increase causes depression.   W. D. H.

The Oxygen Capacity of Blood in Relation to the Concentration of Hæmoglobin. J. H. BURN (*J. Physiol.*, 1913, **45**, 482—488).—No alteration in the oxygen capacity of the blood was discovered when the blood is diluted. Manchot states that it is increased.   W. D. H.

Determination of the Constant of the Differential Blood-Gas Apparatus and the Specific Oxygen Capacity of Blood. JOSEPH BARCROFT and J. H. BURN (*J. Physiol.*, 1913, **45**, 493—497). —This apparatus can be best calibrated by the liberation of a known quantity of oxygen from a standard solution of hydrogen peroxide by potassium permanganate. The constant obtained is then higher than by previous methods. Applying this constant, the specific oxygen capacity of hæmoglobin becomes 401·8, the theoretical figure being 400·8 c.c. of oxygen per gram of iron.
                                                                W. D. H.

The Effect of Exercise on the Dissociation Curve of Blood. JOSEPH BARCROFT, R. A. PETERS, FF. ROBERTS, and J. H. RYFFEL *Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xlv).—The following new terms are introduced. The blood is said to be *mesectic* when the dissociation curve is normal; *pleonectic* when at any given pressure of oxygen the hæmoglobin takes up more of that gas than normal; and *meionectic* when it takes up less. The immediate effect of severe exercise is to shift the curve in the direction of greater acidity, even though the carbon dioxide tension is reduced. After rapid climbing, the curve becomes meionectic; after slow climbing, it remains mesectic.   W. D. H.

The Effect of Altitude on the Dissociation Curve of Blood. JOSEPH BARCROFT, MARIO CAMIS, G. C. MATHISON, FF. ROBERTS, and J. H. RYFFEL (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xlvi).— Although altitudes up to 15,000 feet lower the carbon dioxide alveolar pressure, the blood of the resting subject remains mesectic, for other acids in the blood compensate for the carbon dioxide. Meionexy is brought on by exercise more readily than at the sea level.   W. D. H.

The Effect of Carbohydrate-free Diet on the Dissociation Curve of Blood. JOSEPH BARCROFT, G. GRAHAM, and HAROLD L. HIGGINS (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**).—In three out of five cases the curve remained mesectic, although the carbon dioxide tension fell. In two cases it became pleonectic, and the subjects felt knocked up and faint.   W. D. H.

The Effect of Moist Heat on the Dissociation Curve of Blood. JOSEPH BARCROFT, MARIO CAMIS, G. C. MATHISON, FF. ROBERTS, and J. H. RYFFEL (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xlvii—xlviii).—With the wet bulb at 24·5° the carbonic acid

tension fell (as it often does in factories under similar conditions), and the blood became pleonectic. In all these conditions the subject feels well if his blood is mesectic; but variations in either direction produce symptoms of ill-health. W. D. H.

Sugar Loosely Combined in the Blood. RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, **156**, 110—112. Compare A., 1904, ii, 56; 1907, ii, 562).—The authors have estimated not only the free sugar in the blood of dogs, but also the sugar liberated, after destroying the glycolytic ferment by heating the blood mixed with water at 58° for fifteen minutes, by the addition of emulsin and invertase and keeping the mixture at 39° for forty-five minutes. There is but little or no difference in the amounts of sugar liberated from arterial and venous blood, and but little and in some cases no sugar is liberated from the blood of normal dogs bled for the first time. The amount becomes considerable (up to 50% increase of total sugar) after the physiological equilibrium of the dog has been subjected to marked disturbance by such means as (*a*) severe hæmorrhage, (*b*) intravenous injection of amylase or pancreatin or extracts of liver or pancreas, (*c*) subcutaneous injection of phloridzin. In some cases, also, the intravenous injection of 2 grams of dextrose per kilo. of body-weight was followed by a rise in the amount of sugar liberated by the above method. W. G.

The Behaviour of Blood-Sugar in Normal and Pathological Cases. IV. The Blood-Sugar in Febrile and Dyspnœic Conditions of Man. FR. ROLLY and FR. OPPERMANN (*Biochem. Zeitsch.*, 1913, **48**, 259—267. Compare this vol., ii, 159).—In febrile conditions in man, there is an increase of blood-sugar which at times is quite considerable. There is, however, no parallelism between the increased amount and the rise in the height of the temperature. The hyperglycæmia is caused partly by the hyperthermia and bacterial toxins. In cases of dyspnœa, without high temperatures, where the carbon dioxide content of the blood is increased, hyperglycæmia also occurs. There are, therefore, in certain cases, two distinct causes for increased sugar in the blood, namely, febrile conditions and dyspnœa. Toxic substances, of varied origin, such as tolylenediamine, can also give rise to hyperglycæmia. S. B. S.

The Behaviour of Blood Sugar in Normal and Pathological Cases. V. The Blood-Sugar in Nephritis, Arteriosclerosis, and Diseases of the Nerves. FR. ROLLY and FR. OPPERMANN (*Biochem. Zeitsch.*, 1913, **48**, 268—277).—Inflammation of the kidneys by itself does not give rise to hyperglycæmia. When such occurs in conjunction with inflammation of the kidneys, it is caused by other factors, which are concomitant pathological conditions, such as arteriosclerosis, dyspnœa, uræmic coma, or bacterial and other toxins. There is no parallelism between the hyperglycæmia and the degree of hypertension. In cases of diseases of the nerves the behaviour of the blood-sugar showed great variations, which depend largely on the seat and character of the affection. S. B. S.

Fibrinsæmia. J. O. WAKELIN BARRATT (*J. Path. Bact.*, 1913, 17, 301—322).—If thrombin or thrombokinase is injected into the blood-stream of rabbits, separation of fibrin occurs in the circulating blood; the rate of intravascular clotting varies, and is specially readily produced in the right side of the heart; the circulation is by this means mechanically interfered with.   W. D. H.

The Sodium and Carbonate Ions in the Serum, and the Question of the "Non-diffusible" Alkali. PETER RONA and PAUL GYORGY (*Biochem. Zeitsch*, 1913, 48, 278—290).—The method of compensation dialysis was employed in these experiments, the serum being placed in a dialysing membrane, and surrounded by water containing various amounts of salts, the mixtures being kept at the same hydrogen ion concentration as the serum by means of phosphate mixtures. By analysis, after a definite time the amount of salt in equilibrium with that in the serum was ascertained. It was found that the amount of sodium in equilibrium with that of the serum was 0·3260%, whereas the amount in serum determined directly was 0·3057%. There was therefore practically no non-diffusible sodium. The amount of potassium and sodium in equilibrium was found by dialysis to be 0·9214%, whereas the amounts in serum were 0·8532%. In taking into account these two numbers, the volume occupied by the serum proteins must also be considered. The amount of diffusible carbon dioxide was 0·1270%, and that estimated directly in the serum was 0·1270% in one experiment, and similar numbers were obtained from other series. The greater part of the carbon dioxide is therefore diffusible, although a small part is apparently combined as a carbamido-derivative of the proteins.   S. B. S.

Rate of Regeneration of Anti-substances [Specially Hæmolysin) and Other Constituents of the Blood after Hæmorrhage. R. A. O'BRIEN (*J. Path. Bact*, 1913, 17, 425).—The experiments were made on horses. After bleeding, the constituents of the blood are replaced at differing rates; the volume returns to the normal within forty-eight hours; the proteins commence to be reproduced within twenty-four hours, and the red corpuscles and hæmoglobin within two days. The alterations in leucocytes are irregular, and cannot be correlated with any other factor. The production of anti-substances is as rapid as that of the blood-volume, and suggests that the tissues have a long, persistent habit of forming them in the absence of specific antigens.   W. D. H.

Can Lipoids Act as Antigens? JAMES RITCHIE and J. MILLER (*J. Path. Bact.*, 1913, 17, 429—431).—No evidence was found that lipoids can act in this way.   W. D. H.

Hydrolysis of Glycogen by Diastatic Enzymes. Comparison of Glycogen from Various Sources. ROLAND VICTOR NORRIS (*Biochem. J.*, 1913, 7, 26—42).—On hydrolysis with extract of pig's pancreas, the glycogen is rapidly converted into dextrins and

maltose; the further cleavage of the dextrins is slow and incomplete. The optimum temperature for glycogen hydrolysis is 37°, for starch 40°. When excess of glycogen is present the action is a linear one. The concentration of glycogen has little influence on the initial rate of hydrolysis unless very low concentrations are employed. The action is hindered slightly by the products of hydrolysis; it is favoured by traces of acid. Samples of glycogen from different sources are hydrolysed at different rates at the optimum hydrogen ion concentration; thus, taking dog glycogen as 100, the relative rates of hydrolysis are: rabbit glycogen, 94; oyster, 88; and yeast, 84. The degree of opalescence and the coloration with iodine also vary. The difference may be due to differences in constitution, or to variations in colloidal state. If the glycogens are distinct, the enzymes which affect them should be specific; this is to be tested. W. D. H.

The Secretion of Pancreatic Juice.
Iwawo Matsuo (*J. Physiol.*, 1913, **45**, 447—458).—In the preparation of secretin from the intestinal mucous membrane, boiling with 0·6% sodium chloride is as effective as 0·4% hydrochloric acid; organic acids give a smaller yield. Injection of salt solution into the duodenum does not, however, cause a flow of pancreatic juice as the injection of acid does. Secretin was not obtained from any other organ. If two dogs are in vascular connexion, injection of acid into the duodenum of one evokes a pancreatic flow from the other. After the introduction of hydrochloric acid into the duodenum, the duodenal contents contain secretin. Secretin, however, is not absorbed from the intestinal contents, nor does it produce its effects when given under the skin. The view that secretin and " vaso-dilatin " are identical is negatived. W. D. H.

The Rôle of the Pituitary in Carbohydrate Metabolism.
Lewis H. Weed, Harvey Cushing, and Conrad Jacobson (*Proc. Amer. Physiol. Soc.*, 1912; *Amer. J. Physiol*, **31**, xiii—xiv).—The posterior lobe of the pituitary plays an important part in carbohydrate metabolism, and its action is controlled by fibres in the cervical sympathetic nerve. Stimulation of this nerve, or of the " sugar centre " in the bulb, or of the pituitary body itself, liberates a hormone which causes glycogenolysis and glycosuria, independently of any possible nervous impulse reaching the muscles or abdominal viscera. W. D. H.

Carbohydrate Metabolism in Ducks.
G. B. Fleming (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xliii—xliv).—Partial removal of the pancreas in ducks raises the amount of sugar in the blood, but does not produce glycosuria. Complete extirpation of the organ has a more pronounced effect on the blood, and sometimes leads to glycosuria. Subcutaneous injection of adrenaline after partial extirpation lowers the percentage of sugar in the blood, and in half the experiments produced glycosuria. The respiratory quotient after fasting averaged 0·72; after feeding on maize, 0·93; after

adrenaline, 0·88. This suggests that the effect of adrenaline is to mobilise carbohydrates; its effect passes off rapidly.   W. D. H.

Nitrogen Retention on Feeding with Urea. EMIL ABDER-HALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, 83, 338—346).—Polemical. A reply to Grafe and Turban (this vol., i, 216).   E. F. A.

Protein Metabolism from the Point of View of Blood and Tissue Analyses. VI. Uric Acid, Urea, and Total Non-protein Nitrogen in Blood. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1913, 14, 29—43).—By the authors' new methods it is possible to measure various degrees of nitrogen retention and urea accumulation due to kidney insufficiency with considerable accuracy. Numerous analyses of the uric acid, urea, and total non-protein nitrogen in the blood are presented both in health and disease. The figures show that there is no relationship between the amount of uric acid and that of urea and non-protein nitrogen. Uric acid may accumulate in the blood, even although urea and other nitrogenous waste products are eliminated quite as well as by normal kidneys; the damage to the kidney in gout may thus affect only its power to eliminate uric acid. Apparently very slight kidney damage may affect its power to excrete uric acid.   W. D. H.

The Metabolism of Organic Phosphorus Compounds; Their Hydrolysis by the Action of Enzymes. R. H. ADERS PLIMMER (*Biochem. J.*, 1913, 7, 43—71)—The action of enzymes is summarised in the following table:

	Pancreas.	Liver.	Intes-tine.	Castor oil seeds.	Yeast (zymin).	Bran.
Glycero-phosphoric acid	0	0	+	+		
Hexose-phosphoric ,, ...	0		+	+	*	+
Ethyl dihydrogen phosphate .	0		+			+
Diethyl hydrogen ,,			0	0		
Phytic acid	0	0	0		0	+
Nucleic acid (thymus)	0		+		+ ?	
,, (wheat)			+ /			
,, (meat)	0					
Hydroxymethylphosphinic acid	0		0	0	+ /	0
Phosphoprotein..................	+		+		0	0

The most active tissue is the intestinal mucosa. Phytic acid is attacked readily by bran extract only. Phosphoprotein is the only compound hydrolysed by the pancreas. The other compounds in the list are esters; it is evident that the enzyme which attacks them is not lipase. The question whether the phosphatases are single or specific is discussed, and it is suggested that there are mono- and di-phosphatases. Phytase is specific, and if phytin is decomposed in the intestine, this is due to phytase swallowed with the food. It then enters the body as inositol and phosphoric acid. The work of Fingerling and Gregersen is confirmed, that the animal body can and does synthesise its organic phosphorus compounds from inorganic phosphates.   W. D. H.

The **Rate of Protein Katabolism.** E. PROVAN CATHCART and HENRY HAMILTON GREEN (*Biochem. J.*, 1913, **7**, 1—17).—The rise in the output of nitrogen and sulphur after a protein meal is due to katabolism of the actual material ingested, and not to the displacement of "effete" protoplasm from the tissues. This conclusion is based on the ratio of the sulphur and nitrogen in the urine; after ingesting egg albumin the S : N ratio is 1 : 8, which is nearly the same as that in egg-albumin. The ratio in starvation when all the urinary constituents must arise from the tissues is 1 : 15. The sulphur is more rapidly excreted than the nitrogen; this confirms the view of previous investigators that the sulphur-containing moiety of the protein is the more rapidly katabolised. When protein is superimposed on a low protein diet, a retention of part of the nitrogen takes place. The retained material is apparently stored in the tissues (? muscles) as a pabulum of uniform composition. There was no effect on the output of creatinine.

W. D. H.

The **Metabolism of Lactating Women.** EDWARD MELLANBY (*Proc. Roy. Soc.*, 1913, *B*, **86**, 88—109).—The post-partum excretion of creatine does not depend on the involution of the uterus. After Cæsarian section, involving amputation of the uterus, it may become more marked than in cases in which the uterus is left intact. Rabbits do not excrete creatine at this period; the explanation of this is not obvious. Eating the placenta will not explain the difference, for cows after eating the placenta, excrete large quantities of creatine. The creatine excretion has some relation to the activity of the mammary gland. The rise in the creatine : creatinine ratio in the first few days after delivery corresponds with the increased activity of the milk glands and the development of milk from colostrum. The increase of weight in healthy breast-fed children is roughly proportional to the amount of creatine in the mother's urine. If the activity of the breasts is delayed after childbirth, so also is the excretion of creatine, and later both develop at the same time. Milk suppression from disease is accompanied by a suppression also of creatine excretion. Feeding with caseinogen does not affect the excretion of creatine in parturient women. The post-partum excretion of creatine is dissimilar from that accompanying acidosis and lack of carbohydrates. Lactose and dextrose added to the diet do not affect it. W. D. H.

Nutrition of the Embryonic Chick. I. **The Absorption of Egg-white.** HUBERT W. BYWATERS (*Proc. physiol. Soc.*, 1913; *J. physiol.*, **45**, xl—xli).—During incubation, the proteins of the white are not absorbed as quickly as the water, and the ratio of coagulable to uncoagulable protein remains constant; the free sugar is rapidly absorbed; there is no cleavage of carbohydrate from the protein. W. D. H.

The **Importance of Phosphorus in the Nutrition of Growing Dogs.** ERNST DUBLACH (*Arch. expt. Path. Pharm.*, 1913, **71**, 210—250).—Young dogs fed on a diet poor in phosphorus stop

growing, waste, and die. This, however, is not wholly attributable
to lack of phosphorus. The absence of other unknown constituents
of a diet, possibly of lipoid nature, seems to be a factor, as in
Stepp's experiments. Inorganic phosphates appear to be as advan-
tageous for nutrition as phosphatides.   W. D. H.

Nutritive Value of the Maize Proteins. THOMAS B. OSBORNE
and LAFAYETTE B. MENDEL (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J.
Physiol.*, 31, xvi—xvii).—Zein alone produces speedy decline in the
growth of rats; it can be made adequate for maintenance by adding
tryptophan, or by the addition of another protein. Gliadin suffices
for maintenance, but not for growth. Glutelin is adequate for
both.   W. D. H.

The Influence of Diets upon Growth. F. GOWLAND HOPKINS
and ALLEN NEVILLE (*Biochem. J*, 1913, 7, 97—99).—A criticism of
the work of Osborne and Mendel on the nutrition of young
animals on purified proteins (A, 1912, ii, 271). If these workers
are correct, the accessory factors in diet (so-called vitamines) are
not indispensable. The present experiments do not support this
view. On the Osborne-Mendel diet the animals did not grow; but
an addition to it daily of 2 c.c. of milk produced growth. W. D. H.

Fasting PAUL E. HOWE (*Biochem. Bull.*, 1912, 2, 90—100).—
A general discussion of the subject based on the author's work,
with special reference to fasting as a therapeutic agent. Long fasts
are devoid of benefit, and may be dangerous. Short fasts may be
beneficial in certain cases.   W. D. H.

A New Method of Drying Tissues and Glands. JACOB
ROSENBLOOM (*J. Biol. Chem.*, 1913, 14, 27—28). - Instead of using
anhydrous salts, the employment of calcium carbide is recom
mended [compare Masson, T., 1910, 97, 857].   W. D. H.

A New Type of Artificial Cell. E. NEWTON HARVEY (*Biochem.
Bull.*, 1912, 2, 50—52).—The manner of making cells of about the
size of those in the body is described; they contain an aqueous
solution of lecithin enclosed in a fine protein membrane, and are
suitable for permeability and other biochemical studies. W. D. H.

Pigment of the Corpus luteum. HEINRICH H. ESCHER (*Zeitsch.
physiol. Chem.*, 1913, 83, 198—211).—Willstatter and Escher (A.,
1912, i, 125) have shown that lutein, the yellow pigment of egg
yolk, belongs to the xanthophyll group of pigments soluble in
alcohol. It is now proved that the yellow pigment of the *Corpus
luteum* belongs to the carrotene group, $C_{40}H_{56}$, soluble in light
petroleum. The process of purification adopted in obtaining 0·45
gram of pigment from 146 kilos. (about 10,000 ovaries) is described.
The carrotene is indistinguishable from that obtained from carrots
or from green leaves. The yellow pigment of fat is considered to
belong to the same class of pigments.   E. F. A.

The Lipoids of the White and Grey Matter of the Human Brain at Different Ages. J. LORRAIN SMITH and W. MAIR (*J. Path. Bact.*, 1913, **17**, 418—420).—Five brains were analysed by the methods previously described. The results are given in tables. In the adult the percentage of total lipoids is twice as great in the white as in the grey matter, but the cerebroside is higher, and the phosphatide much lower, than in the grey matter. At birth, there is a low percentage of phosphatides, and more of other lipoids, and the composition is nearly the same throughout the brain. By the age of two, the condition in the adult is nearly, but not quite, reached.   W. D. H.

Chemical Changes in Nerve During the Passage of a Nerve Impulse. SHIRO TASHIRO (*Proc. Amer. Physiol. Soc*, 1912; *Amer. J. Physiol.*, **31**, xxii—xxiii).—The author states that he has constructed an apparatus by which he is able to detect and estimate carbon dioxide in amounts as small as 0.0000001 gram. Resting nerve gives off this gas, and the amount is increased when the nerve is stimulated.   W. D. H.

The Utilisation of Sugars by the Normal Heart. HUGH MACLEAN and (Miss) IDA SMEDLEY (*J. Physiol.*, 1913, **45**, 462—469). —Locke's method for the isolated heart was employed. The utilisation of sugar by the heart is not confined to dextrose; mannose is also used, and so is lævulose, especially in the dog's heart. Maltose, lactose, and sucrose are not utilised, and galactose very slightly. In the cat, sugar does not disappear from the circulating fluids until about three hours after perfusion commences; it is assumed that the reserves in the heart are utilised first. It was found difficult to secure asepsis during the experiments.   W. D. H.

The Behaviour of the Diabetic Heart towards Sugar. HUGH MACLEAN and (Miss) IDA SMEDLEY (*J. Physiol.*, 1913, **45**, 470—472). -The normal power to consume sugar is absent or nearly so in the heart of the depancreatised dogs; the power can be sometimes restored by the addition of pancreatic extract. These experiments confirm those of Knowlton and Starling.   W. D. H.

The Storage and Release of Glycogen. KUNTOMI ISHIMORI (*Biochem. Zeitsch.*, 1913, **48**, 332—346).—The methods of experiment were both chemical (estimation of glycogen) and histological (with use of Best's carmine method). Rabbits were employed. It was found that the course of disappearance of glycogen produced by starvation was different from that produced by *piqûre*. In the former case, it disappears from the periphery of the lobe, towards the centre, and glycogen as such could not be detected outside the liver cells. In the latter case, all the liver cells are affected alike, and glycogen could be detected in the lymph spaces and circulation. Intravenous infusion of dextrose and lævulose caused an increase in the glycogen content of the liver. This was not the case with lactose, galactose, and sucrose.   S. B. S.

The Character of the Fat Formation in Organs after Phosphorus Poisoning. HANS LEO (*Biochem. Zeitsch.*, 1913, **48**, 297—301).—The author recapitulates the evidence in favour of the new formation of fat in the liver of animals poisoned with phosphorus, which probably exists in this organ in addition to the transported fat.   S. B. S.

Fat Formation under the Influence of Phosphorus. HANS LEO and W. TRASCHENNIKOV (*Biochem. Zeitsch.*, 1913, **48**, 302—312). —The majority of the experiments were carried out with the livers of rabbits, part of which were incubated under precautions for strict asepsis in Ringer's fluid alone as a control, and part under the same conditions with the addition of phosphorus. After incubation, the amount of ether-soluble substances, or higher fatty acids, were estimated. In eight experiments the addition of phosphorus caused an increase in fatty substances. In three experiments the results were of a negative character.   S. B. S.

Fat Formation in the Surviving Liver. HANS LEO and C. BACHEM (*Biochem. Zeitsch*, 1913, **48**, 313—327).—The effect produced on the fat content of livers by perfusing both foodstuffs and toxic substances through the surviving organs was investigated. Livers both of cold-blooded and warm-blooded animals were used. and the Langendorff apparatus was employed. In five experiments with foodstuffs (sugar or nutrose in Ringer's fluid), the results indicated fat formation, whereas in four experiments the results were negative. All the experiments with livers of warm-blooded animals yielded a positive result. The addition of alcohol and potassium arsenite showed no fat formation In four experiments with diphtheria toxin, one gave a negative, one a doubtful result, and two others indicated fat formation in the liver. Out of fourteen experiments with phosphorus water, ten gave negative, and four positive results. The general result indicates that there is no new fat formation in the liver as the result of the action of phosphorus, although two of the experiments with livers of warm-blooded animals indicated an increase in fats. It is suggested that in the case of cold-blooded animals, the rate of fat formation is too slow for it to be possible to obtain an increase in the amount of fat under the conditions of experiment employed.   S. B. S.

The Delayed Heat-Production of Muscles Stimulated in Oxygen. ARCHIBALD V. HILL (*Proc. physiol. Soc*, 1912; *J. Physiol*, **45**, xxxv—xxxvii).—By improved methods the author's previous conclusion is confirmed that heat-liberation occurs largely (probably 40%) after muscular contraction; oxygen is mainly of use in repair. The action of oxygen is rapid.   W. D. H.

The Physico-chemical Basis of Striated Muscle Contraction. II. Surface Tension. WILLIAM N. BERG (*Biochem. Bull.*, 1912, **2**, 101—110. Compare this vol., i, 132).—Bernstein's calculations

of the surface energy changes in contracting muscles are criticised. The energy expended is far greater than any changes in surface tension can furnish. The use of mathematics in biology is regretted, if the treatment, as it so generally does, lacks definiteness; formulæ are often stated with no information as to their use or application to the problem under discussion. W. D. H.

Osmotic and Colloidal Imbibition by Muscle. REINHARD BEUTNER (*Biochem. Zeitsch.*, 1913, **48**, 217—224).—The experiments were carried out with the gastrocnemius muscle of frogs, and the changes after various treatments are measured by estimating the gain or loss of weight of the muscles. It was found that the addition of proteins to salt solutions in which the muscles are immersed has no appreciable effect on the water exchange between the tissues and the surrounding fluid. If the stimulability of muscle is destroyed by treatment with acid, its ordinary osmotic functions can still be detected, even for a long period after the loss of stimulability. If, on the other hand, the stimulability is destroyed by heat coagulation, the osmotic properties are lost.
S. B. S.

The Chemical Pathology of Muscle. The Influence of Disuse Atrophy in the Partition of Nitrogen and Phosphorus in the Muscle. GEORGE GRUND (*Arch. expt. Path. Pharm.*, 1913, **71**, 129—141).—Full analytical details of paralysed in comparison with healthy muscle are given. The most important result appears to be an increase of phosphorus in protein union in the paralysed muscles.
W. D. H.

The Creatine Content of Normal Muscle and its Relation to Urinary Creatinine. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1913, **14**, 9—26).—The creatine content in muscle is constant in a given animal, but differs in different animals; the percentages are 0·52 for the rabbit, 0·45 for the cat, 0·37 for the dog, and 0·39 for man. The creatinine elimination bears a distinct relation to the muscular creatine content. W. D. H.

Occurrence of Alizarin in the Shell of the Crab. FRIEDRICH KORNFELD (*Chem. Zeit.*, 1913, **37**, 71).—A reply to Grandmougin (this vol., i, 132) describing further experiments which support the view expressed previously (*Chem. Zeit.*, 1912, **36**, 59) that crab-shells contain alizarin. T. A. H.

Normal Presence of Bromine in Human Organs. A. LABAT (*Compt. rend.*, 1913. **156**, 255—258. Compare Pribram, 1907, ii, 111).—The various organs of human beings, who had not taken bromine medicinally for several years, were pulped, dried, and incinerated with calcined magnesia, and the ash examined for bromine by the method of Denigès and Chelle (this vol., ii, 72). Bromine could not be detected in the kidney, spleen, liver, heart, or blood serum or coagulum of the four subjects examined, but in

all cases was found in the brain, thyroid gland, and urine. The amount of bromine present in the thyroid gland is considerably less than the iodine.   W. G.

The Presence and Distribution of Manganese in Animal Organs. GABRIEL BERTRAND and FLORENTIN MEDIGRECEANU (*Ann. Inst. Pasteur*, 1913, **27**, 1—11).—Manganese has been found in all the animal products examined with the exception of the white of egg. The variations in amount are only small in a given organ of a given species. There is, as a rule, very little difference in the content of manganese in organs of animals of different species belonging to the same class (birds, fishes, mammals). Amongst functional organs the highest amount of manganese has been found in the uterus of birds (0·786—2·201 mg. per 100 grams). Next in order are the liver, then the kidneys. The organs of birds are richer than those of mammals. Smallest amounts are found in muscular tissue, nervous tissue, and (least of all) the lungs, which only contain 0·006 to 0·023 mg. per 100 grams. The grey nervous matter contains more than the white, and heart muscle more than the muscles of the limbs. The mucous membranes contain more than the underlying muscular tissue. Feathers and nails contain relatively large quantities of manganese (0·111 to 3·214 mg. per 100 grams), whereas the teeth contain little. Milk contains very little manganese, and in the egg the whole of the metal is in the yolk. The general results indicate that manganese plays some physiological rôle as a catalyst.   S. B. S.

The Origin of Oxalic Acid in the Animal and Human Organism. LESLAW WEGRZYNOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 112—142).—Proteins have no influence on the formation of oxalic acid in the body, neither have carbohydrates and fats (also glycerol). The ordinary articles of diet have no influence, direct or indirect, on oxalic acid formation. The organism evidently has a very limited capacity to form this acid at all.   W. D. H.

Histones and Nucleohistones. Their Detection in the Fluids of the Organism. GEORGES PATEIN (*J. Pharm. Chim.*, 1913, [vii], **7**, 55—60).—A description is first given of the characters of histones and nucleohistones, and by the application of Gonbau's method it is shown that these substances do not occur in the blood serum of man or the horse, or in ascitic fluid containing chyle. The conclusion is drawn therefore that histones and nucleohistones, which have only been found in such organs as the thymus and the spleen, are fixed there, and cannot be carried away by the body fluids.

Acetoglobulin tested in the course of these experiments was found to contain only traces of phosphorus, and sometimes none. T. A. H.

Relation of Pulse Pressure to Renal Secretion. ROBERT A. GESELL (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol*, **31**, xxviii—xxix).—In dogs alterations of the arterial pressure, espe-

cially if suddenly produced, cause diminution in the secretion of urine, and if albuminuria is present, this is increased. W. D. H.

Excretion of Nitrogen after Ligaturing the Renal Arteries. J. D. PILCHER (*Proc. Amer. physiol. Soc.*, 1912 ; *Amer. J. Physiol.*, 31, xii—xiii).—Tying one branch of each renal artery has no effect; but if three-fourths of the arterial supply is cut off, anorexia and loss of weight occur, and the nitrogen output is greater than the intake. The urine secreted contains neither protein nor casts. W. D. H.

Beri-Beri. The Action of Certain Purine and Pyrimidine Derivatives. CASIMIR FUNK (*J. Physiol.*, 1913, 45, 489—492) — Certain purine and pyrimidine derivatives have marked beneficial effect on pigeons suffering from polyneuritis; no relation, however, between the action and chemical structure can be discovered. Experiments with allantoin suggest that pigeons are not able to convert uric acid into allantoin. W. D. H.

Colloidal Nitrogen in the Urine of a Dog with a Breast Tumour. MAX KAHN and JACOB ROSENBLOOM (*Biochem. Bull.*, 1912, 2, 87—89).—Töpfer states that the urine of cancer patients is rich in "extractive substance," which includes "colloidal nitrogen." The colloidal nitrogen was more abundant in a dog with a tumour in the breast than in normal dogs. The nature of the tumour was doubtful. W. D. H.

The Comparative Mineralisation of Cancareous and Relatively Healthy Portions of the Liver. ALBERT ROBIN (*Compt. rend.*, 1913, 156, 334—336).—Cancareous portions of liver are richer in total inorganic matter than healthy parts, and whilst some of the inorganic constituents, namely phosphorus, sodium, potassium, magnesium, and silicon, are in excess, others, namely, calcium and iron, are deficient. A similar deficiency in calcium and iron is found in tuberculous lungs, potassium again being in excess. Whilst in the cancareous liver relatively more sodium than potassium is fixed, the reverse is true in the case of a tuberculous lung. From the experimental results, it seems probable that silicon, phosphorus, sodium, potassium, and magnesium are agents of neoplastic cell construction, not specifically for cancer, whilst iron and calcium are rather agents of organic defence. W. G.

Hæmatogenous Jaundice. GEORGE H. WHIPPLE (*Proc. Amer. physiol. Soc.*, 1912 ; *Amer. J. Physiol.*, 31, xi—xii).—If hæmoglobin is given intravenously to a normal dog, it appears in the urine, and one or two hours later bile pigment occurs there also. The same occurs after an Eck fistula, and also when the hepatic artery is tied in addition. This is taken to prove that bile pigments can be formed in the blood, probably by the agency of the endothelial cells. W. D. H.

The Swelling of Connective Tissues. EDWIN HAUBLRRISSER and FRITZ SCHONFELD (*Arch. expt. Path. Pharm*, 1913, **71**, 102—128). —Martin Fischer's theory of œdema renders necessary an investigation of the part played by different ions (for example, in Ringer's solution) in causing swelling. A large number of observations on this line are recorded, and the principal conclusion is stated to be that sodium ions do not act differently from the others. The experiments were in the main performed on the ligamentum nuchæ.   W. D. H.

Antagonism between Salts and Anæsthetics. III. Parallel Decrease in the Stimulating, Permeability-increasing, and Toxic Actions of Salt Solutions in the Presence of Anæsthetics. RALPH S LILLIE (*Amer. J. Physiol*, 1913, **31**, 255—287. Compare A., 1912, ii, 280, 468).—Pure isotonic sodium chloride solutions produce in *Arenicola* larvæ stimulation of the muscles, arrest of ciliary action, and a general toxic action. These results are lessened or prevented by anæsthetics; the stimulating action and permeability increase undergo a parallel diminution. The essential effect of anæsthetics is an alteration in the plasma membranes of the cells affected. The degree of resistance of these membranes is intimately dependent on the state of their lipoid constituents.
                                                      W. D. H.

Behaviour of Mercury in the Human and Animal Organism on the Usual Therapeutic Methods of Application. New Method for the Estimation of Mercury in Urine and in the Tissues. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, **83**, 249—303).—Contains a critical summary of the methods of estimating mercury in urine with a full bibliography. A method is described of destroying the urine by evaporating with potassium chlorate and hydrochloric acid and so converting the mercury into chloride. The solution is filtered and electrolysed in a special apparatus between a cathode of gold foil and a gas carbon anode. The mercury is deposited on the gold, which is rinsed, dried and weighed, and heated to volatilise the mercury, the weight of which is determined by difference.

The skin is equally able to take up volatile and non-volatile mercury ointments; the ointment base has an accelerating influence on the resorption. The separation of mercury in the urine has been studied after internal administration, and also after intramuscular and intravenal injection of mercury salts In the latter case the separation is materially faster. The addition of potassium iodide to the mercury salt is shown to diminish the excretion of the mercury.   E. F. A.

The Influence of Alcohol on Reflex Action in the Frog. IDA H. HYDE, RUTH SPRAY, and IRENE HOWAT (*Amer. J. Physiol*, 1913, **31**, 309—317).—The reflexes investigated were from certain skin areas. If the dose of alcohol used is sufficient to produce any effect at all, it is always a depressed or slowed response, never the opposite.   W. D. H.

Glyconeogenesis. II. The Formation of Dextrose from Valeric and Heptoic Acids. A. I. RINGER and L. JONAS (*J. Biol. Chem.*, 1913, **14**, 43—52).—In phloridzinised dog-, the administration of formic acid leads to no increase in the output of dextrose; butyric and hexoic acids increase the excretion of acetoacetic and β-hydroxybutyric acids, but not that of sugar. Valeric and heptoic acids give rise to dextrose, probably because propionic acid is an intermediate substance in their katabolism, after undergoing β-oxidation. Fatty acids with an uneven number of carbon atoms can therefore give rise to dextrose. W. D. H.

The Fate of Indole-ethylamine [3-β-Aminoethylindole] in the Organism. ARTHUR J. EWINS and PATRICK P. LAIDLAW (*Biochem. J.*, 1913, **7**, 18—25).—If 3-β-aminoethylindole (Ewins, T., 1911, **99**, 270) is perfused through the surviving liver of rabbits and cats, it is converted into indoleacetic acid. If it is given by the mouth to dogs, 30% of it is excreted as *indole-3-acetylglycine*,

$$\underset{NH\cdot CH}{\overset{C_6H_4}{\diagdown}}{>}C\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H \quad (picrate, \text{ m.p. } 145°)$$

(for which the authors suggest the name *indoleaceturic acid*), which is formed from indoleacetic acid by combination with glycine. Neither 3-β-aminoethylindole nor indoleacetic acid affects the output of kynurenic acid. W. D. H.

Influence of Intraperitonal Injection of Adrenaline on the Partition of Urinary Nitrogen in a Dog. JACOB ROSENBLOOM and WILLIAM WEINBERGER (*Biochem. Bull.*, 1912, **2**, 123—127) — The nitrogen partition was not affected. W. D. H.

Action of Drugs on the Lungs. DENNIS E. JACKSON (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xxvi—xxvii).—Pilocarpine causes bronchial constriction, which is relieved by adrenaline. The nerve endings are sensitive to the latter drug after atropine. Agaricine slightly depresses the constrictor nerve-endings. In small doses the pilocarpine effect is followed by dilatation, but the second effect does not occur if the suprarenals are tied off. Tyramine also causes dilatation, but this is a secondary adrenaline effect also. Choline hydrochloride acts like adrenaline, so also do trimethylamine hydrochloride and 3:4-dihydroxy-phenylethylmethylamine in less degree. W. D. H.

The Pharmacological Susceptibility of the Peripheral Vascular Tonus of the Frog. HANS HANDOVSKY and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1913, **71**, 89—101).—The Läwen Trendelenburg preparation of the frog was used. Vaso-constrictors fall under three types: (1) adrenaline, which affects post-ganglionic nerve fibres; (2) nicotine, which affects pre-ganglionic and ganglionic structures; and (3) barium, which affects the muscular fibres. The dilators, tyramine, histamine, and Witte's peptone, all

act in the same way. They dilate the vessels after adrenaline is used; tyramine hinders nicotine action. Choline acts as a dilator.
W. D. H.

Nicotine and Calcium Salts. W. BURRIDGE (*Proc. physiol. Soc.*, 1912; *J. Physiol.* **45**, xxxvii—xxxix).—Isotonic solutions of sodium oxalate, sulphate, fluoride, pyrophosphate, and citrate produce a slow tonic contraction of the frog's sartorius muscle. This is attributed to the removal of calcium. Nicotine produces, in addition, twitchings, which are largely abolished by curare. W. D. H.

The Effect of Strychnine on Frogs without Heart and Lymph Hearts. SAMUEL J. MELTZER (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xix—xx).—Abel considers that the effect of drugs in a frog without a heart is brought about by the continued activity of the lymph hearts. This is not so for strychnine. Strychnine convulsions set in after thirty to fifty minutes when the lymph hearts are all destroyed. W. D. H.

Muscle Physiology. Action of Veratrine on Striated Muscles in Warm-blooded Animals. G. QUAGLIARIELLO (*Zeitsch. Biol.*, 1913, **59**, 441—468).—Veratrine causes two contractions, the second of which lasts longer. It also causes fibrillary twitchings in small doses. Variations in the curves obtained with varying doses are illustrated by reproductions of the tracings. W. D. H.

The Action on Man of Vapours of Technical and Hygienic Importance. XXX. Nitric Acid. KARL B. LEHMANN and LUDWIG DIEM (*Arch. Hygiene*, 1913, **77**, 311—322).—The toxic symptoms on animals of air contaminated by nitric acid are not particularly characteristic, and are similar to those produced by other irritant substances, such as hydrogen chloride, sulphur dioxide, etc. Three cats died in the respiration chamber in 35 to 120 minutes in the presence of 0·5 to 0·73 mg. of the acid to 1 litre of air. Two animals recovered after doses of 0·43 to 0·5 mg., and one survived until the next day with a dose of 0·88 mg. after remaining in the presence of the air-acid mixture for 200 minutes. The post-mortem examination showed no marked inflammation of the mucous membrane of the eyes, nose, or mouth, or œdema of the glottis. The bronchial passages were, however, hyperæmic, and the lungs exhibited œdema. S. B. S.

The Action on Man of Vapours of Technical and Hygienic Importance. XXXI. The "Nitrous Gases": Nitric Oxide, Nitrogen Dioxide, Nitrous and Nitric Acids. KARL B. LEHMANN and HASEGAWA (*Arch. Hygiene*, 1913, **77**, 323—368).—A summary is given of a number of cases in the literature describing the toxic symptoms produced in man by the "nitrous gases," which act essentially as a mixture of nitrous and nitric acid. Attention is called to the great differences as regards the susceptibility of

individuals to the poison. Experiments were carried out on animals with gas made by the action of nitric acid on copper. This was diluted with hydrogen, and mixed with air. An apparatus is figured to show how this was accomplished, and how samples of the air to which the animals were exposed could be removed for analysis. The analysis was accomplished by passing the air, first, over hydrogen peroxide, when the nitrous acid was oxidised to nitric acid, and the total nitrate, both preformed and produced by oxidation of the nitrous acid, was precipitated by nitron. The gas unabsorbed in the first absorption apparatus was passed through a second apparatus containing potassium iodide, and the iodine set free was titrated by thiosulphate solution. The general result of the experiments with mixtures of equimolecular proportions of nitrous and nitric acid is to show that the mixture acts as if all the nitrogenous products were in the form of nitric acid (see preceding abstract). In the majority of the animal experiments the toxic symptoms were different from those in man. These were generally only slight inflammatory reactions on the mucous membranes, œdema of lungs, in certain experiments, methæmoglobin formation, and indications of an action on the central nervous system. The temporary recovery after removal from the noxious vapours, with subsequent relapse, as is observed in the case of man, occurred only seldom in the case of animals. Experiments on man (Hasegawa), but carried out only with small doses of the noxious vapours, indicated that the symptoms were similar to those on animals. Various experiments were also carried out on the reduction of nitrate to nitrite by animal tissues, on the distribution of nitrites in tissues after injection into the trachæa, and on the toxic effect of nitrite administration. It was shown that the quantities of nitrite which produced severe symptoms after inhalation were far smaller than the quantities necessary to produce characteristic nitrite poisoning. The injurious effects in the inhalation experiments are to be ascribed to the production of the lung œdema. In man there is a latent period before the injurious effects are observed, which is generally absent in the case of animals.

S. B. S.

The Natural Resistance of the Hedgehog towards Certain Poisons M. A. WILLBERG (*Biochem. Zeitsch.*, 1913, **48**, 157—174).— It was found that the hedgehog could tolerate a dose of atropine sulphate 248 times larger (calculated per kilo. of body-weight) than that tolerated by man. The tolerance towards morphine hydrochloride was 245 times as greater; towards nicotine, 29 times; towards potassium arsenite, 10 times; towards curare, 7 times; towards potassium cyanide, 6 times; towards mercuric chloride, 4 times; and towards phenol, twice as great. There was no difference in the tolerance towards strychnine nitrate.   S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Bacterial Reduction of Sulphates to Sulphides. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 165—169).—Sasaki and Otsuka (A., 1912, ii, 475), working with 21 races of bacteria in pure culture, were unable to reduce sulphate to sulphide, and further state that bacteria produce no hydrogen sulphide from taurine.

Positive evidence is now quoted showing that in a great variety of cases bacteria relatively readily reduce sulphates to hydrogen sulphide.   E. F. A.

Bio-chemistry of Micro-organisms VII. The Fermentation of Formic Acid by Bacillus Kiliense in a Medium of Constant Composition. HARTWIG FRANZLN and F. EGGER (*Zeitsch. physiol. Chem.*, 1913, **83**, 226—228).—The paper consists chiefly of data obtained from experiments carried out on the same lines as those in which *Bacillus prodigiosus* was used (A., 1912, ii, 669). A slight production of formic acid occurs during the early stages of growth, after which fermentation takes place. The results show great divergence in the behaviour of the organism in different series of cultures, and general conclusions cannot be drawn.   H. B. H.

Action of Uranium Salts and Metallic Uranium on the Pyocyanic Bacillus. HENRI AGULHON and ROBERT SAZERAC (*Compt. rend.*, 1913, **156**, 162—164. Compare this vol., i, 143).—A study of the influence of uranium salts, soluble and insoluble, on the pyocyanic bacillus, the amount of pyocyanin formed being estimated colorimetrically, the culture medium used being hydrolysed serum. The toxic dose of uranyl acetate is 1 in 500, and of uranyl nitrate, 1 in 200. Doses of from 1 in 50,000 to 1 in 1000 are distinctly favourable, as was shown by the colour test, and also by the thickness of the microbic film produced. With insoluble uranium compounds, potassium or ammonium uranate, doses of 1 in 1000 to 1 in 100 gave an increase of 100% in the yield of pyocyanin, whilst in the case of the metal itself doses of 1% gave a decided growth within twenty-four hours in a medium to which the bacillus was not accustomed. The medium being neutral, this last effect could not be due to any of the uranium passing into solution, and finally favourable action was produced on the microbe in sealed tubes, the uranium being outside, thus pointing to the radioactivity of the uranium as being the cause of the increased growth in this and the previous cases.   W. G.

Influence of Salts of Uranium and Thorium on the Development of the Tubercle Bacillus. PAUL BECQUEREL (*Compt. rend.*, 1913, **156**, 164—166).—Radioactive salts of uranium and thorium behave physiologically like many other non-radioactive salts. They each have an optimum dose, which produces the

maximum growth of the bacillus, above which they begin to exert a toxic effect, uranyl nitrate being much more toxic than thorium nitrate. A dose of 1 in 2500 of the former has a marked inhibitory influence, whilst the same dose of the latter seems to be its optimum as regards increased microbic growth.   W. G.

Indole Reaction. HUGO ZIPFEL (*Centr. Bakt. Par.*, 1913, i, 67, 572—584. Compare A., 1912, ii, 793).—The contradictory results often yielded by the indole test may be attributed to unsuitability or variability of the medium. The use of a composite tryptophan medium with or without the addition of glycerol or dextrose is recommended, whereby trustworthy results can be obtained in twenty-four to forty-eight hours. Comparative tests of a large number of strains of certain pathogenic and non-pathogenic bacteria were made, and consistent results obtained with the various strains of each species of organism. The p-dimethylaminobenzaldehyde test for indole was found to be the most trustworthy.   H. B. H.

Mechanism of Alcoholic Fermentation. S. KOSTYTSCHEV (*Ber.*, 1913, 46, 339. Compare Kostytschev, A., 1912, ii, 589; Kostytschev and Hübbenet, *ibid*, 1912, ii, 860).—A claim for priority against von Lebedev (this vol., i, 144), in demonstrating that acetaldehyde is formed during the fermentation of sugar in the presence of zinc chloride, and, further, that acetaldehyde is reduced to ethyl alcohol by living yeast and various yeast preparations.   H. W.

Alcoholic Fermentation. III. Conditions Regulating the Formation of Acetaldehyde during the Fermentation of Hefanol (Yeast). S. KOSTYTSCHEV (*Zeitsch. physiol. Chem.*, 1912, 83, 93—104. Compare A., 1912, ii, 589; also Kostytschev and Hübbenet, A., 1912, ii, 860).—A reply to the criticisms of Neuberg and Kerb (A., 1912, ii, 973). Paracetaldehyde is very easily decomposed into acetaldehyde on distillation with traces of acid.

Autofermentation of yeast is a true alcoholic fermentation of the yeast glycogen; acetaldehyde is one of the products of the change. When fermentation of hefanol is effected in presence of sufficient methylene-blue to render the active reducing agent inoperative, acetaldehyde is formed as the normal reduction of acetaldehyde to ethyl alcohol is restricted.   E. F. A.

Biochemical Synthesis of Alkylglucosides (α-Glucosides) by means of a Ferment (α Glucosidase) contained in Air-dried Bottom Yeast. α-Ethylglucoside. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and MARC BRIDEL (*Compt. rend.* 1913, 156, 168—170).—The authors have obtained α-ethylglucoside in a crystalline form, $[\alpha]_D$ +150·64°, by the action of a ferment, extracted from bottom yeast by water, on a dilute alcoholic solution of dextrose containing at least 65% of water by volume. The yield with respect to the dextrose used was 33%, and the glucoside was readily hydrolysed in aqueous solution by the same ferment, which they name α-glucosidase.   W. G.

Assimilation of Nitrate and Nitrite. V. Oskar Baudisch and Erwin Mayer (*Ber*, 1913, **46**, 115—125. Compare A, 1911, ii, 523; 1912, ii, 286, 1202).—When a dilute formaldehyde–potassium nitrate solution is exposed to sunlight a mixture of nitrous oxide and hydrogen, together with some carbon dioxide and monoxide, is evolved. In a formaldehyde-potassium nitrite solution, in addition, small quantities of nitric oxide are also formed. This originates from the decomposed nitroxyl NOH, a substance which does not exist as gas.

Angeli's salt, ONa·N:NO·ONa, decomposes on warming in aqueous solution into nitrous and nitric oxides and ammonia.

Solutions of potassium nitrite in either formaldehyde or methyl alcohol which have been exposed to light contain methylamine and, further, formic acid, hyponitrous acid, and hydroxylamine In addition an alkaloidal compound similar to nicotine and containing a pyrrole ring is formed. Whereas in the assimilation of carbon the carbonic acid is reduced to carboxylic acid by the yellow and red rays of the spectrum, in the assimilation of nitrogen the blue, violet, and ultra-violet rays cause the reduction of nitrates to nitroxyl.   E. F. A.

The Influence of Uranium and Lead on Vegetation. Julius Stoklasa (*Compt. rend.*, 1913, **156**, 153—155).—Uranyl nitrate added in small amounts to pot cultures of *Melilotus albus* already supplied with suitable fertilisers, had a favourable effect on the total yield of dry matter, the optimum quantity being 2·5 kilos. of uranium per hectare of soil. With 20 kilos. per hectare there was no indication of any toxic effect. The results with lead nitrate on oats and on *Polygonum fagopyrum* are of the same order, but the amount of lead which has an injurious effect is much less than in the case of uranium, the addition of lead nitrate at the rate of 8 kilos. per hectare being detrimental to the total crop in each case.   W. G.

The Cause of Growth in Plants. I. G. A. Borovikov (*Biochem. Zeitsch.*, 1913, **48**, 230—246). — The author reviews M. Fischer's experiments on the influence of acids, bases, and salts on various imbibition processes, for example, in gelatin and muscle. The view has been expressed by Fischer and others, that the phenomena of growth are determined, not so much by the osmotic properties of the cell, as by the capacity of the various colloids to imbibe water. The capacity is affected differently by various ions contained in the solution. The method of experiment employed by the author to investigate the various factors was as follows. Seedlings (six days old) of *Helianthus annuus* were placed in tubes which hung vertically in cylinders containing various solutions, and after intervals of three, six, and twelve hours and longer, removed, and the rate of growth was measured and compared with the rate of growth in pure water. The influence of various acids, bases, and salts on the rate of growth during short intervals was thus ascertained. It was found that acids accelerate the growth during the

first period, and if salts are present at the same time, the growth in the presence of both acid and salt is diminished as compared with that in acid alone.   The effect of the various ions and cations was studied in some detail, and attention is drawn to the parallelism between their influence on the rate of growth and their general effect on imbibition processes.   The experiments, generally, confirm the conception of the relationship between imbibition processes and growth.   S. B. S.

Presence of Formaldehyde in the Sap of Green Plants. FRANCESCO ANGELICO and G. CATALANO (*Gazzetta*, 1913, **43**, i, 38—43). —The formaldehyde which is supposed to be an intermediate product in the photosynthesis of starch in green plants has never been demonstrated in the sap with certainty.   The test for formaldehyde with atractylin (compare Angelico, A., 1910, i, 403) is not only very sensitive, but also specific.   The leaf-sap and its distillate of eleven species of green plants tested in this way showed the presence of formaldehyde, whilst the same products from six species previously kept for twenty-four hours in the dark gave no reaction. Three non-chlorophyllic, parasitic plants were also tested, and formaldehyde was found to be absent.   The results are therefore in complete agreement with the usual theory of photosynthesis.

R. V. S.

The Function of the Carboxylase in Plants.   W. ZALESKI and ELIZABETH MARX (*Biochem. Zeitsch.*, 1913, **48**, 175—180).—The seeds employed were sterilised with mercuric chloride, then dried and powdered.   The seeds of *Lupinus luteus* decompose free pyruvic acid as readily as they do its sodium salt.   Pea seeds, on the other hand, decompose the free acid less readily than its salt, a fact due probably to the alkalinity of the powder.   Seeds of *Vicia faba* only weakly attack the free acid, although they readily attack the sodium salt.   Lupine seeds can also attack pyruvic acid in a vacuum. Both pyruvic acid and its sodium salts inhibit the carbon dioxide production of the immature seeds.   Acetaldehyde could be detected in the experiments with both lupine and pea seeds when pyruvic acid was present.   It could be also detected, but in very much smaller quantities in the control experiments, in which the acid was absent.   The authors call attention to the parallelism of the actions of the seed carboxylase and of zymase, and discuss the rôle played by pyruvic acid in degradation of sugars and the production of ethyl alcohol.   S. B. S.

Rôle of Oxydases in the Formation of the Anthocyan Pigments of Plants.   FREDERICK KEEBLE and EDWARD FRANKLAND ARMSTRONG (*J. of Genetics*, 1912, **2**, 277—311.   Compare A, 1912, ii, 673).—The methods previously described for the localisation of oxydases have been extended to a variety of plants.   Peroxydase is shown to be more widely distributed than the organic peroxide which activates it.   The very general phenomenon of browning presented by dried plants is regarded as an indication of the presence

)f a complete oxydase. Exposure of plants to darkness leads to the formation of peroxide and to an increase of peroxydase. The bearing of these facts on the general metabolism in the plant is discussed.

E. F. A.

Colloidal Chlorophyll and the Shifting of the Absorption Bands in the Leaves of Living Plants. D. IVANOVSKI (*Biochem. Zeitsch.*, 1913, **48**, 328—331).—Herlitza has drawn the conclusion, from spectroscopic observations, that chlorophyll exists in the colloidal form in living plants. The author gives a table of extinction coefficients, and shows that those of the chlorophyll of the leaf fall between those of colloidal chlorophyll and of an alcoholic solution of the pigment. He draws attention to the fact that the chlorophyll in leaves exists, not evenly distributed, but in the chloroplasts, and that the absorption spectrum of the leaf combines the characters of an absorption and reflection spectrum. He shows that the absorption spectrum of the leaf can be closely imitated by the addition of electrolytes to colloidal chlorophyll. According to the size of the granula thus produced, the absorption band is shifted thereby towards the ultra-red. S. B. S.

Plant Fats. CARL THOMAE (*J. pr. Chem*, 1913, [ii], **87**, 144) — The fatty and waxy constituents of yeast, rose blossoms, and the skins of apples, grapes, peaches, potatoes, lemons, gherkins, and other parts of plants may be readily isolated in a state of purity by heating under diminished pressure. F. B.

The Non-Specificity of Zinc as a Biological Catalyst for the Culture of Aspergillus niger. CHARLES LEPIERRE (*Compt. rend.*, 1913, **156**, 258—261).—The author has tried the effect of replacing the zinc in Raulin's solution by cadmium on the cultivation of *Sterigmatocystis nigra*, and his results are not in accord with those recently put forward by Javillier (compare this vol., i, 235). On the contrary, he finds that cadmium replaces zinc perfectly in Raulin's solution, and, like it, plays a very energetic part in the rapid growth of the plant, being fixed by the plant. Further, he finds that zinc is not a specific catalyst for this culture, but can be replaced by other elements chemically analogous to it.

W. G.

Attempts to Substitute Glucinum for Magnesium and Zinc in the Culture of Sterigmatocystis nigra (Aspergillus niger). MAURICE JAVILLIER (*Compt. rend.*, 1913, **156**, 406—409. Compare this vol., i, 235).—A reply to Lepierre (preceding abstract). From further experiments the author maintains that glucinum cannot replace magnesium or zinc in the culture medium for *Aspergillus niger*, the magnesium being necessary as a nutrient and the zinc as a catalyst. He suggests that the difference between his and Lepierre's results may be due to the conditions of their culture media, or hereditary influences on the cultures. W. G.

Replacement of Zinc by Glucinum in the Culture of Aspergillus niger. CHARLES LEPIERRE (*Compt. rend.*, 1913, **156**, 409—411. Compare this vol., i, 235; preceding abstracts).—The results obtained are in direct opposition to those of Javillier (previous abstract). The author finds that the zinc in Raulin's liquid can be replaced by glucinum without affecting the weight of crop finally obtained from the culture of *Aspergillus niger* thereon, except that the maximum is somewhat retarded. This retardation is, however, only relative, and diminishes as the plant adapts itself to the new medium. Time, adaptation, and easy access of air play an important part in these cultures. The glucinum is fixed by the plant. W. G.

Formation of Urea by Two Moulds. ROBERT FOSSE (*Compt. rend.*, 1913, **156**, 263—265. Compare A., 1912, ii, 1203).— The author has isolated urea in small quantities in the form of its xanthhydrol derivative from the expressed juice of mycelium gathered from the surface of Raulin's liquid and also from *Aspergillus niger* grown on a solution in which ammonium nitrate has replaced the chloride in Raulin's liquid. *Penicillium glaucum* similarly contains small quantities of urea in its cells. From his results the author draws the conclusion that the principal factor in ureogenesis is a process of oxidation, and not, as at present supposed, a diastatic oxidation. W. G.

The Nitrogenous Constituents of Lime Juice. CASIMIR FUNK (*Biochem. J.*, 1913, **7**, 81—86).—In view of work on beri-beri, in which the physiological importance of certain substances (probably pyrimidine derivatives) has been shown, lime juice was examined in reference to scurvy. Lime juice cures scurvy, and also contains an antineuritic substance. Pyrimidine substances in general prolong life in birds with polyneuritis. No anti-scorbutic substance, however, was separated out from lime juice. The investigation was hampered by the guinea-pigs refusing to take oats, a diet which leads to scurvy in these animals. Milk prevents oats from causing scurvy, even though the proteins are removed. The anti-scorbutic material in milk is destroyed by a high temperature. Its unstable character may have led to the negative results with lime juice. Several new compounds were, however, separated from lime juice; one, $C_{13}H_{24}O_3$, needles, m. p. 97 –100°, apparently belongs to the terpene group; one, $C_6H_7O_2N_5$, crystalline plates, m. p. 282° (corr.), to the purine group; one, $C_9H_{18}O_6N_2$, microscopic spherolites, m. p. 188—189° (decomp.), to the pyrimidine group; and a fourth to the choline group; the latter crystallised in cubes, and gave a platinichloride, $(C_8H_{17}O_2N)_2H_2PtCl_6$, m. p. 220°. The phosphotungstic and silver nitrate precipitates were mainly examined. W. D. H.

Constituents of Apples. CARL THOMAE (*J. pr. Chem.*, 1913, [ii], **87**, 142—144).—The substance, m. p. above 200°, previously isolated by the author (A., 1911, ii, 920) from apple-skins may be separated

by treatment with ether into an insoluble substance of high melting point, and a waxy substance crystallising in needles, m. p. 68·5°. On distillation under diminished pressure, the oil obtained by extracting the skins with ether yields a crystalline substance of low melting point having an odour of apples and a yellow oil which readily solidifies. The behaviour of the skins on distillation is also described.   F. B.

Leaves of Barosma venusta. HAROLD R. JENSEN (*Pharm. J.*, 1913, [iv], **36**, 60—61).—This material from Cape Province, South Africa, yielded 1·1% of volatile oil, $D_{15.5}^{15.5}$ 0·8839, $a_D^{20} + 0°30'$, n_D^{20} 1·4967, of greenish-yellow colour, and having acid value 2·4 and saponification value 13·4. On treatment with potassium hydroxide solution, 16% of the oil dissolved, and a further 4% was absorbed by a solution of neutral sodium sulphite. The oil was separated into nine fractions by distillation under reduced pressure, and the physical constants, ultimate composition, and reactions with bromine, sodium, and phenylhydrazine of each fraction are recorded. From a consideration of these data the following composition is tentatively suggested for the oil: myrcene, 35; chavicol, 16; myrcenol and sesquiterpene alcohols, 15; methylchavicol and anethole, 15; sesquiterpenes, esters, ketones, aldehydes, and acids, 19%. The leaves also contain oleoresin, acid resins, colourless glucosides, fat, carbohydrates, and a little tannin. The results show that these leaves do not contain the same constituents as the commercial buchus derived from *B. betulina* and *B. serratifolia*, and that they cannot be used in medicine in place of these.
                                                        T. A. H.

Constituents of Lycoperdon bovista. JAN J. BLANKSMA (*Chem. Weekblad*, 1913, **10**, 96—100).—Fresh specimens of the edible mushroom, *Lycoperdon bovista*, contain trehalose, tyrosine, a substance with m. p. 165°, chitin, and leucine, all previously isolated (compare Bourquelot, *J. Pharm. Chim.*, 1907, [vi], **25**, 382; Bamberger and Landsiedl, A., 1903, ii, 567; 1905, ii, 852). The trehalose is converted by trehalase, invertase, and diastase into reducing sugars, these ferments being present in the mushrooms. The darkening in colour of mushrooms is explained by the conversion of tyrosine into melanin, a black substance, under the influence of tyrosinase It is possible that leucine is converted into *iso*amylamine, and the tyrosine into *p*-hydroxylphenylethylamine, a substance of very poisonous character. It is known that old specimens of *Lycoperdon bovista* are poisonous. The author recommends the preparation of glucosamine hydrochloride by boiling mushrooms with dilute hydrochloric acid after elimination of proteins, fats, and calcium salts.   A. J. W.

Organic Chemistry.

Notes on Mine Gas Problems. GEORGE A. BURRELL (*J. Ind. Eng. Chem.*, 1913, 5, 181—186).—The author gives an account of the various problems met with in connexion with mine gases, interpolating from time to time some of the data accumulated by the Bureau of Mines with respect to the explosibility and physiological effects of mine atmospheres, and to flame extinction and after-damp.

The lower explosive limit of mixtures of air and methane is confirmed to be 5·5% methane. The presence of carbon dioxide alters this explosive limit, but even 10% of carbon dioxide raises it only to 6·6%. Reduction in the volume percentage of oxygen also raises the explosive limit. Harger has suggested that a small reduction in the oxygen percentage and a small increase in the carbon dioxide percentage in mine air will suffice to produce an atmosphere incapable of supporting combustion, and consequently an atmosphere in which explosions and gob fires cannot occur, but the data obtained by the Bureau of Mines indicate that the figures given by Harger are much too low, both with respect to the increase in carbon dioxide and diminution in oxygen.

When acetylene is used in the miner's lamp, the flame resembles the ordinary wick flame burning in pure air, when the oxygen content of the air decreases to 16—16·5%; this behaviour of the flame can be used as a guide to men venturing into workings containing black damp and less oxygen than the percentage given. The ordinary miner's lamp is extinguished when the oxygen falls to about 16·5—17%; the extinguishing of the flame is shown to be due to deficiency in oxygen and not to the presence of carbon dioxide.

Reference is made to the following subjects: Effect of vitiated air on the luminosity of miner's lamps (compare Haldane, *Colliery Guardian*, Oct. 25th, 1912); high velocity of air currents in mines; distribution of after-damp; intrusion of natural gas into mines, etc. Analyses are also given of mine-gas mixtures containing explosive and other proportions of methane, and of samples of after-damp atmospheres which show the large amount of carbon monoxide (white-damp) present shortly after an explosion. T. S. P.

Solvents for Acetylene. JOSEPH H. JAMES (*J. Ind. Eng. Chem.*, 1913, 5, 115—120).—An investigation of the solvent powers for acetylene of a number of organic liquids shows that those containing the carbonyl group are generally the best solvents. Organic acids must be excluded, however, the hydroxyl in the carboxyl group seeming to inhibit the solvent action of the carbonyl. The presence of the carbonyl group is not sufficient, of itself, to account for the solubility, since methylal and acetal are very good solvents.

It is found that acetaldehyde fulfils all the industrial requirements for an acetylene solvent. T. S. P.

Preparation of Dimethylacetylene [Crotonylene] and Ethyl-acetylene from Carbides. CARL WILLI SCHLUCHTER (D.R. P. 253802).—When methyl alcohol is heated with an alkaline earth carbide during four days at 60—120° under a pressure of 50 atmospheres, or during six days in a closed tube at 200° it yields a mixture of crotonylene (Δ^β-butinene), $CMe\vdots CMe$, b. p. 28°, and ethylacetylene [Δ^a-butinene], $CEt\vdots CH$, b. p. 18°.   F. M. G. M.

Δ^{ayc}-Heptatriene and Related Substances. CORNELIS J. ENKLAAR (*Chem. Weekblad*, 1913, 10, 187—189. Compare this vol., i, 243).—A discussion of the influence of structure on the possibility of solidifying unsaturated hydrocarbons. By cooling with liquid air several butadienes and related substances have been converted into the solid state.   A. J. W.

Vinylacetylene. RICHARD WILLSTÄTTER and THEODOR WIRTH (*Ber.*, 1913, 46, 535—538).—By the action of dimethylamine in benzene solution on the dibromide of butadiene, $a\delta$-tetramethyl-diamino-Δ^β-butylene, $NMe_2 \cdot CH_2 \cdot CH\vdots CH \cdot CH_2 \cdot NMe_2$, is obtained. The use of an indifferent solvent, such as benzene, is essential; with alcohol numerous secondary reactions take place.

When the corresponding diquaternary ammonium base is distilled in a vacuum it is decomposed, and vinylacetylene, $CH\vdots C \cdot CH\vdots CH_2$, is obtained.

$a\delta$-*Tetramethyldiaminobutylene* is a colourless oil with a narcotic odour, b. p. 171—172°/723 mm., 65—65·5°/17 mm., D_4^0 0·8198. The *picrate* forms needles, m. p. 222—223°; the *aurichloride* separates in crystalline needles, m. p. 201° (decomp.); the *platinichloride*, $2H_2O$, crystallises in long, rhombohedric prisms, m. p. 227—228°, whilst the *dimethiodide* forms prisms, decomp. 270°.

Vinylacetylene [$\Delta^{a\gamma}$-*buteninene*] melts to a colourless liquid, b. p. 2—3°/729 mm., and has an odour like acetylene. It forms a greenish-yellow copper salt and a colourless, crystalline silver salt, which explodes when heated.   E. F. A.

A Catalytic Method of Isomerisation of Alkyl Chlorides and Bromides. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1913, 156, 658—659. Compare A., 1905, i, 677).—Barium chloride or thorium chloride at 250° causes the decomposition of primary alkyl chlorides or bromides into ethylene hydrocarbons and hydrogen chloride or bromide. These then recombine, when passed over pumice stone at 200°, giving, not the original haloid, but the isomeric chloride or bromide. The resulting liquid is submitted to fractional distillation, thus separating any of the original unchanged substance.   W. G.

Trichloroethylene and Some of its Derivatives. JACOB BOESEKEN [with C. E. KLAMER and J. G. DE VOOGT] (*Rec. trav. chim.*, 1913, 32, 15—22).—Unsuccessful attempts have been made to bring trichloroethylene and tetrachloroethylene into reaction with benzoyl chloride, sulphur chloride, phosphorus chloride, thionyl chloride, and

sulphuryl chloride respectively in the presence of aluminium chloride. Charred products were obtained, except in the case of tetrachloroethylene and sulphuryl chloride, when hexachloroethane was isolated, owing to the decomposition of sulphuryl chloride into sulphur dioxide and chlorine and union of the latter with tetrachloroethylene.

Barium monochlorosulphoacetate, C_2HO_5ClSBa, was isolated from the product of the action of fuming sulphuric acid (containing 10% SO_3) on trichloroethylene at 88°.

When trichloroethylene was added drop by drop to a mixture of nitric acid (D 1·5) and concentrated sulphuric acid, cooled by a freezing mixture of salt and ice, and the action interrupted as soon as the temperature of the product rose but slowly when removed from the freezing mixture, dichloroacetic acid was obtained, together with a *substance*, $C_2HO_8N_2Cl_3$, b. p. 32°/36 mm., which, when preserved, became converted into colourless, very hygroscopic needles, which were insoluble in, or decomposed by, the ordinary solvents, and had mol. wt. 194 in nitrobenzene solution. When heated with hydrochloric acid, this substance yielded small amounts of nitric oxide and carbon dioxide, but neither hydroxylamine nor oxalic acid could be detected. Alcoholic potassium hydroxide decomposed it according to the equation: $C_2HO_8N_2Cl_3 + 7KOH = 3KCl + 2K_2CO_3 + 4H_2O + N_2$. With zinc and cold dilute sulphuric acid it gave a quantitative yield of ammonia. It did not give Liebermann's reaction. In view of the above properties, the annexed formula is tentatively proposed for it. H. W.
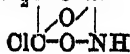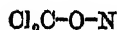
$$\begin{array}{l} Cl_2C\text{-}O\text{-}N \\ \quad |\diagup O| \\ ClO\text{-}O\text{-}NH \end{array}$$

Elimination of Water from Pinacolyl Alcohol. Tertiary Butylethylene. W. FOMIN and N. SOCHANSKI (*Ber.*, 1913, **46**, 244—248).—Pinacolyl alcohol was converted by Couturier (A., 1893, i, 245) into a bromide, which, when treated with solid potassium hydroxide, gave a mixture of $\beta\gamma$-dimethyl-Δ^β-butylene (compare Zelinsky and Zelikov, A , 1902, i, 2) with a small quantity of a hydrocarbon, b. p. 56—59°, which was described as *tert.*-butyl ethylene. The latter compound has now been prepared from pinacolyl alcohol by Tschugaev's method and has other properties.

The potassium derivative is prepared by adding the alcohol to potassium *tert*-amyloxide (compare Tschugaev, A., 1905, i, 167) and then treated with carbon disulphide and methyl iodide. The *methyl pinacolyl xanthate*, C_6H_{12}·O·CS·SMe, b. p. 100°/12 mm., D_4^{10} 1·0228, decomposes at 160—175°, and the purified *tert.-butylethylene* [$\gamma\gamma$-*dimethyl-Δ^α-butylene*], CMe_3·CH⫶CH$_2$, is a colourless liquid, having b. p. 41·2°/760 mm., D_4^{10} 0·6549, and n_D 1·37667. On oxidation with permanganate, acetone is not obtained, the chief product being $\alpha\alpha$-dimethylpropionic acid, whilst reduction with hydrogen in presence of platinum black results in the formation of $\beta\beta$-dimethylbutane.

J. C. W.

Decomposition of Heptyl Alcohol at 220° in the Presence of Finely Divided Nickel. JACOB BÖESEKEN and G. H. VAN SENDEN (*Rec. trav. chim.*, 1913, **32**, 23 38).—The authors have repeated the

experiments described by van Beresteyn (A., 1911, i, 761), who obtained heptyl alcohol and a substance which he regarded as *n*-hexylene, by the reduction of heptaldehyde according to the general method of Sabatier and Senderens. Heptyl alcohol, under similar circumstances, was found to yield *n*-hexylene, carbon monoxide, and hydrogen, the course of the actions being represented by the equations: $C_6H_{13}\cdot CHO + H_2 = C_7H_{15}\cdot OH$. $C_7H_{15}\cdot OH = C_6H_{12} + CH_3\cdot OH$. $CH_3\cdot OH = CO + 2H_2$. On theoretical grounds, the authors consider this interpretation to be improbable, and are led to the conclusions : (1) that heptyl alcohol, in the presence of finely divided nickel at 220°, is decomposed into heptaldehyde and hydrogen ; (2) that, particularly in the presence of an inert gas, the heptaldehyde is converted into *n*-hexylene, hydrogen, and carbon monoxide ; (3) that *n*-hexylene combines with a considerable proportion of the liberated hydrogen to form *n* hexane, and that, in the presence of an excess of hydrogen, all the *n*-hexylene undergoes reduction ; (4) that heptaldehyde is not reduced in the presence of carbon dioxide, and only slightly reduced in an atmosphere of hydrogen ; (5) that *n*-hexylene (mixed with *n*-hexane) is best obtained by the decomposition of heptaldehyde by nickel at 220° in a current of carbon dioxide, and (6) that *n*-hexane is obtained by the catalytic decomposition of heptyl alcohol or heptaldehyde by nickel at 220° in a current of hydrogen.

Heptyl alcohol was obtained by the reduction of heptaldehyde dissolved in glacial acetic acid by means of sodium amalgam. Small quantities of s-*di-n-hexylethyleneglycol* [*n-tetradecane-ηθ-diol*], b. p. 218°/14 mm., m. p. 69—70°, were obtained as by-product.

Heptyl alcohol, when passed over nickel at 220° in a current of hydrogen, yielded about 62% *n*-hexane, 17% of a mixture of heptyl alcohol and heptaldehyde, and carbon monoxide. In a current of carbon dioxide, however, it yielded about 14·5% *n*-hexylene, 31% *n*-hexane, 24% of a mixture of heptyl alcohol with a little heptaldehyde, carbon monoxide, and hydrogen, the change being represented by the equation : $3C_7H_{15}\cdot OH = 2C_6H_{14} + C_6H_{12} + 3CO + 4H_2$.

Heptaldehyde, at 220° in a current of carbon dioxide, gave about 24% *n*-hexylene, 29% *n*-hexane, 16% unchanged heptaldehyde, carbon monoxide, hydrogen, and possibly a trace of formaldehyde. The quantities of the products obtained agreed with the equation : $100C_6H_{13}\cdot CHO = 45C_6H_{12} + 55C_6H_{14} + 100CO + 45H_2$. At 180°, the course of the reaction was similar.

n-Hexane was not affected when passed over nickel at 220° in a current of carbon dioxide.   H. W.

aδ-Oxide from Undecyl Alcohol. N. A. LOGGINOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 136—145)—The action of zinc chloride or 50% sulphuric acid on undecyl alcohol results in displacement of the double linking of the alcohol and formation of the aδ-*oxide*,

$$CH_3\cdot[CH_2]_6\cdot CH{<}^{OH:CH}_{O—CH_2},$$ b. p. 219—222°, D_0^0 0·8641 (or 0·8667), D_0^{17} 0·8522, D_0^{18} 0 8538.

When zinc chloride is used, the oxide is accompanied by an unsaturated *alcohol*, $C_{11}H_{22}O$, b. p. 243—246°, which forms a crystalline *phenylurethane*, $C_{18}H_{27}O_2N$, m. p. 49·5°, and is being further investigated. T. H. P.

Action of αβ-Dichloroethyl Ether on Mixed Magnesium Derivatives. ROBERT LESPIEAU and BRESCH (*Compt. rend.*, 1913, **156**, 710—712).—αβ-Dichloroethyl ether condenses readily with magnesium derivatives of ethyl and allyl bromides and acetylene, giving products somewhat difficult to purify. The *compound*,
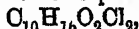
$$C_{10}H_{16}O_2Cl_2,$$

obtained from the acetylene derivative is a colourless liquid, b. p. 136—137°/12 mm., and is probably a mixture of two *cis-* and *trans-*isomerides (compare Dupont, A., 1910, i, 85). On bromination in chloroform, it yields two *dibromides*, $C_{10}H_{16}O_2Cl_2Br_2$, separable by their varying solubility, the less soluble one having m. p. 107—108°, and the other m. p. 71—72°. These are also probably *cis-* and *trans-*isomerides. W. G.

Compounds of Ethyl Phosphite with Silver Haloids. ALEXANDER E. ARBUZOV and A. V. KARTASCHOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 79—81).—Derivatives of tervalent phosphorus of the form PR_3 or $P(OR)_3$ form compounds with cuprous and platinous haloids, and the authors find that ethyl phosphite forms similar compounds with silver haloids. These compounds form colourless, ribbon-like crystals, their melting points being: $P(OEt)_3,AgCl$, 4·5—5·5°; $P(OEt)_3,AgBr$, 40—40·5°; $P(OEt)_3,AgI$, 81—83°. T. H. P.

Uranium Formate. WILLIAM OECHSNER DE CONINCK and ALBERT RAYNAUD (*Bull. Soc. chim.*, 1913, [iv], **13**, 221—223).—Uranium formate is a deliquescent, yellow salt, readily soluble in water. Attempts to estimate the water of crystallisation were unsuccessful, owing to the ready loss of formic acid from the salt on prolonged desiccation. When calcined in a closed vessel, the salt leaves a residue of pure uranous oxide, but, if an open vessel is used, traces of a higher oxide are formed. Similar results were previously obtained with uranium oxalate (A., 1912, i, 535).

When boiled with a large quantity of water, uranium formate is hydrolysed, hydrated uranium trioxide, $UO_3,2H_2O$, separating as a yellow precipitate, which is converted by calcination into the green oxide, U_3O_8.

Uranium formate was exposed to diffused daylight during three months in the presence of methyl alcohol. A brown deposit of uranium oxide was thereby obtained, and the strongly acid methyl alcoholic solution was found to contain methyl formate.

Very little decomposition occurred in similar circumstances in the presence of ethyl alcohol. Very little formic acid was liberated, whilst the residue contained only small amounts of mono- and di-hydrated uranium trioxide mixed with unchanged uranium formate. H. W.

Preparation of Halogen Formic Esters. EMANUEL MERCK (D.R.-P. 254471).—The following halogen formic esters in addition to those previously described (this vol., i, 5) have now been prepared. *Dimethylethylcarbinyl chloro-formate*, a liquid which decomposes at 20° and cannot be distilled in a vacuum ; the homologous *methyldiethylcarbinyl chloro-formate* has similar properties.   F. M. G. M.

Distillation and Sublimation of Ammonium Salts under Diminished Pressure. RICHARD ESCALES and HANS KOEPKE (*J. pr. Chem*, 1913, [ii], 87, 258—279).—Of the normal salts examined the formate (*s*, 90—140°), acetate (*s*, 90°), thiocyanate (*d*, 165°), cyanate (*s*, 160—190°), nitrite (*s*, 70°), and sulphite (*s*, 70—120°) distil or sublime under a pressure of 10 mm. without decomposition, whilst the propionate (*d*, 70—75°), butyrate (*d*, 70—80°), glycollate (*d*, 160°), lactate (*d*, 140—150°), benzoate (*s*, 60—130°), and salicylate (*s*, 90—150°) are converted into the corresponding acid salts, NH_4HX_2 ; the temperatures at which distillation or sublimation occurs are given in brackets (*s* denotes sublimation ; *d*, distillation).   When heated to 300°/10 mm., ammonium sulphate and persulphate lose ammonia, yielding the acid salts; ammonium thiosulphate sublimes at 70°/10 mm., the sublimate consisting of ammonium sulphite.   Ammonium carbonate undergoes complete dissociation, whilst carbamide and thiocarbamide sublime in .the form of ammonium cyanate and thiocyanate respectively.   Of the acid salts, NH_4HX_2, the acetate (*d*, 67°), propionate (*d*, 73°), butyrate (*d*, 78°), glycollate (*d*, 160°), lactate (*d*, 145°), benzoate (*s*, 60—130°), salicylate (*s*, 90—150°), and hydrogen carbonate distil or sublime unchanged at 10 mm.

A mixture of normal or acid ammonium acetate and propionic acid in molecular proportions distils at 66—68°/10 mm., yielding the acid *ammonium* salt, $CH_3 \cdot CO_2 \cdot NH_4, C_2H_5 \cdot CO_2H$, which forms very deliquescent crystals, m. p. 42—43°, and is converted by distillation with butyric acid into the *ammonium* salt, $CH_3 \cdot CO_2 \cdot NH_4, C_3H_7 \cdot CO_2H$. This has m. p. 41°, b. p. 72—74°/10 mm., and is also obtained by distilling normal or acid ammonium acetate with butyric acid.   F. B.

Decomposition of Certain Acid Chlorides by Aluminium Chloride. JACOB BOESEKEN (*Rec. trav. chim.*, 1913, 32, 1—14) ·· In continuation of the work of Böeseken and Prins (A., 1910, i, 152; 1911, i, 173), the action of aluminium chloride on the chlorides or sulphonyl chlorides of a number of halogenated acids has been investigated.   Normal results were obtained with acid chlorides which did not contain hydrogen or a benzene group, but, in the presence of the latter, the reaction appeared to be complex, giving resinous products from which no definite compound could be isolated.

[With P. HASSELBACH.]—Monochloroacetyl chloride and aluminium chloride yielded a hygroscopic, crystalline *compound*,
$$CH_2Cl \cdot COCl, AlCl_3,$$
which, when heated alone or with carbon tetrachloride, evolved hydrogen chloride, leaving a charred residue.   Carbon monoxide could not be detected in the gas evolved.   When heated in chloroform solution at 80°, a small quantity of a *substance*, m. p. about 175°, was obtained, to
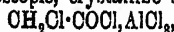
which no definite composition could be assigned. Similarly, aluminium chloride and chlorofumaryl chloride or $a:\beta:\beta:\beta$-tetrachloropropionyl chloride yielded only charred or resinous products, from which a definite compound could not be separated.

[With (Mlle.) S. VAN DER TAS]—*p*-Chlorobenzenesulphonyl chloride and aluminium chloride gave resinous products. The gases evolved contained hydrogen chloride and, generally, sulphur dioxide.

[With W. J. P. PELLE.]—*p*-Bromobenzenesulphonyl chloride and aluminium chloride yielded a crystalline additive product,

$$C_6H_4Br\cdot SO_2Cl,AlCl_3,$$
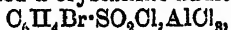
which, when heated at 150—200°, evolved sulphur dioxide and hydrogen chloride, and left a brown resin.

[With P. HASSELBACH.]—*Trichloroacrylyl chloride*, b. p. 158°/760 mm., was obtained by the action of thionyl chloride on trichloroacrylic acid. When mixed with aluminium chloride in carbon disulphide solution, it yielded the *compound*, $CCl_2:CCl\cdot COCl,AlCl_3$, which, when heated in a current of dry air, gave only trichloroacrylyl chloride mixed with a little aluminium chloride, but no carbon monoxide. In the presence of aluminium chloride, trichloroacrylyl chloride reacted with benzene and its homologues to form quantitative yields of ketones of the type $R\cdot CO\cdot CCl:CCl_2$, only the chlorine atom attached to the carbonyl group being replaced.

Pentachloropropionyl chloride, m. p. 42°, obtained from the preceding chloride by the action of chlorine in sunlight, when heated with aluminium chloride at 60° evolved carbon monoxide and carbonyl chloride, leaving a residue from which hexachloroethane and tetrachloroethylene were isolated, decomposition occurring according to the equations: (I) $CCl_3\cdot CCl_2\cdot COCl = CO + C_2Cl_6$. (II) $CCl_3\cdot CCl_2\cdot COCl = COCl_2 + C_2Cl_4$. When treated with aluminium chloride in the presence of benzene, *pentachloropropiophenone*, $COPh\cdot CCl_2\cdot CCl_3$, m. p. 83°, was obtained when the reaction was continued until one molecule of hydrogen chloride had been evolved. When, however, reaction was continued until two molecules of hydrogen chloride had been evolved, tetrachloroethylene and benzophenone were formed. The presence of the latter may be due to dissociation of pentachloropropionyl chloride into tetrachloroethylene and carbonyl chloride, and condensation of the latter with benzene, or pentachloropropiophenone may be decomposed by aluminium chloride into tetrachloroethylene and benzoyl chloride. The odour of the latter is perceptible when pentachloropropiophenone is warmed with a little aluminium chloride.   H. W.

Montanic Acid and its Derivatives. HUGH RYAN and JOSEPH ALGAR (*Proc. Roy. Irish Acad.*, 1913, **30**, 97—105. Compare A., 1909, i, 629).—The authors have prepared a series of derivatives of montanic acid, the formulæ of which are in agreement with the formula, $C_{29}H_{58}O_2$, for montanic acid itself, thus confirming the previous work of Ryan and Dillon (A., 1909, i, 629), and Easterfield and Taylor (T., 1911, 99, 2302), in contrast to that of Holl (*Zeitsch angew. Chem.*, 1900, **13**, 556), von Boyen (A., 1902, i, 72), and Eisenreich.

Methyl montanate, prepared by boiling montanic acid with methyl

alcohol in the presence of sulphuric acid, crystallises in white, curved needles, m. p. 66°. The similarly crystallised *ethyl* and n *propyl* esters have m. p. 64—65° and 63·5° respectively.

Dimethylheptacosylcarbinol, $C_{27}H_5$,·CMe_2·OH, obtained from methyl montanate and magnesium methyl iodide, has m. p. 63—64°, whilst the corresponding *diethyl* and *diphenyl* derivatives melt respectively at 59—60° and 58°. When ethyl montanate is treated with *p*-bromotoluene and the resulting product subjected to steam distillation, the residue is found to consist of the unsaturated *hydrocarbon*, $C_{27}H_{54}$·$C(C_6H_4Me)_2$, m. p. 47°. When, however, the steam distillation is omitted and the product purified by repeated crystallisation from alcohol, it can be separated into two portions, the major part consisting of the above hydrocarbon, the minor part of *di-p-tolylheptacosyl-carbinol*, m. p. 51—52°. The action of an ethereal solution of magnesium α-naphthyl bromide on ethyl montanate appears to yield a mixture of *di-α-naphthylheptacosylcarbinol*, m. p. 57—58°, and, probably, *α-naphthyl-heptacosyl ketone*, $C_{27}H_{55}$·CO·$C_{10}H_7$, m. p. 51—53°. These substances can be readily separated, since the former dissolves very sparingly in hot methyl alcohol, in which the latter is readily soluble.

Unsuccessful attempts were made to isolate *montanyl chloride* in the pure state by the action of phosphorus tri- or penta-chloride on montanic acid. The product obtained had m. p. 63—65°. It was transformed by concentrated aqueous ammonia into *montanamide*, m. p. 109°, small quantities of a *substance*, probably montanonitrile, m. p. 60—65°, being simultaneously formed.

Attempts to prepare ceryl alcohol from montanic acid were unsuccessful, owing to the difficulty of isolating *heptacosylmethylurethane* from the product of the successive action of bromine and sodium methoxide on montanamide. The converse operation (the preparation of montanic acid from ceryl alcohol by the malonic ester synthesis) could not be effected, since cerylmalonic ester could not be obtained from ceryl iodide and sodiomalonic ester under the most varied conditions. *Ceryl iodide*, $C_{26}H_{51}I$, m. p. 55—56°, was obtained by the action of iodine and red phosphorus on ceryl alcohol.   H. W.

Action of Thionyl Chloride on Certain Lactones. PHILIPPE BARBIER and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], 13, 223—229).—A critical survey of the action of thionyl chloride on organic substances is given. The authors have investigated the effect of boiling certain γ-lactones (1 mol.) in benzene solution with thionyl chloride (1·1 mol.). The product of the reaction was poured into excess of methyl or ethyl alcohol and subsequently examined in the form of its methyl or ethyl ester. In these circumstances, thionyl chloride transforms the γ-lactones employed (except coumarin) into esters of γ-hydroxy-acids according to the scheme :

$$R·\overset{|}{C}H·CH_2·\overset{|}{C}H_2 \xrightarrow{SOCl_2} R·\overset{|}{C}H·CH_2·CH_2·COCl \xrightarrow{2C_2H_5OH}$$
$$O\text{————}CO \qquad\qquad O·SOCl$$

$$R·\overset{|}{C}H·CH_2·CH_2·CO_2Et + SO\overset{OEt}{\underset{Cl}{<}} + HCl.$$
$$OH$$
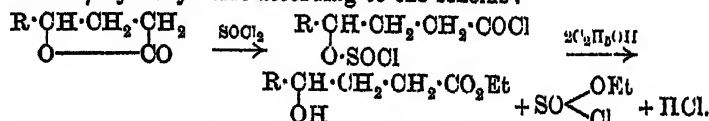
γ-Valerolactone was transformed into ethyl γ-hydroxyvalerate,

b. p. 80—81°/12 mm. (compare Neugebauer, A., 1885, 651), from which a phenylurethane could not be obtained.

γ-Phenyl-γ-butyrolactone, m. p. 37—38°, b. p. 175—176°/11 mm. (Jayne, A., 1883, 472; Fittig and Leoni, A, 1898, i, 196), was prepared by the condensation of bromo-acetophenone with ethyl sodiomalonate and saponification of the crude product with alcoholic sodium hydroxide at 160°. At the high temperature employed, the latter substance probably acted as a reducing agent. In addition, small quantities of benzoylpropionic acid and of a neutral *substance*, m. p. 190—192°, probably a dilactone (annexed formula), were obtained. When acted on successively by thionyl chloride and ethyl alcohol, γ-phenyl-γ-butyrolactone yielded *ethyl γ-hydroxy-γ-phenylbutyrate*, b. p. 158—160°/17 mm.
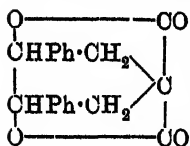
Coumarin did not react with thionyl chloride under the conditions employed. H. W.

Action of Thionyl Chloride on Certain Lactonic Acids. PHILIPPE BARBIER and RENÉ LOCQUIN (*Bull. Soc. chim*, 1913, [iv], 13, 229—236. Compare preceding abstract).—The experimental conditions chosen were the same as those previously described (*loc. cit.*). In these circumstances, thionyl chloride does not cause a rupture of the lactonic grouping, the product of the reaction being the lactonic acid chloride. This result is not influenced by the use of an excess of thionyl chloride.

Methylparaconyl chloride, b. p. about 142°/10 mm., obtained by the action of thionyl chloride on methylparaconic acid, was converted by methyl alcohol into *methyl methylparaconate*, b. p. 145—146°/11 mm.

In similar circumstances, terebic acid slowly yielded the corresponding chloride, b. p. 143°/12 mm., from which *methyl terebate*, b. p. 148—149°/17 mm, was obtained.

ββ-Dimethylbutyrolactone γ carboxylic acid (Perkin and Thorpe, T., 1899, 75, 56) gave the corresponding chloride, which, when treated with methyl alcohol, yielded the *methyl* ester, b. p. 149—150°/12 mm.

Similarly, terpenylic acid formed terpenyl chloride, methyl terpenylate, b. p. 145—147°/15 mm., and ethyl terpenylate, m. p. 37·5°, b. p. 174—177°/15 mm. Fittig and Levy (A., 1890, 873) give b. p. 305°/ordinary pressure, whereas Simonsen (T, 1907, 91, 187) found 169—171°/15 mm.

Phenylparaconyl chloride, prepared by the action of thionyl chloride on anhydrous phenylparaconic acid, m. p. 106°, 115°, or 121° (compare Jayne, A., 1883, 473; Fittig and Röders, A., 1890, 621) yielded, when decomposed by water, the acid, m. p. 99°. With methyl alcohol it yielded *methyl phenylparaconate*, m. p. 69—70°, b. p. 211°/14 mm. In the case of phenylparaconic acid, small quantities of polyphenylcrotonic acid, m. p. 179°, were also isolated.

The authors have attempted unsuccessfully to repeat the previously recorded transformation of terebic and phenylparaconic acids into the

anhydrides of *cis*-3 : 3-dimethyl*cyclo*propane-1 : 2-dicarboxylic acid and *cis*-3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid (A., 1911, i, 722) under the action of thionyl chloride. They now attribute this result to the presence of some impurity in the specimen of thionyl chloride used, and point out that the substance is frequently contaminated with phosphoryl chloride, stannic chloride, sulphur trioxide, etc., to the presence of which the irregular results frequently obtained by the application of the reagent are ascribed.   II. W.

$\gamma\gamma\gamma$-Trichloro-β-hydroxybutyric Acid and $\gamma\gamma\gamma$-Trichloro-crotonic Acid. KARL VON AUWERS and M. SCHMIDT (*Ber*, 1913, 46, 487—494. See following abstract).—$\gamma\gamma\gamma$-Trichloro-β-hydroxy-butyric acid, m. p. 118—119° (von Thurnlackh, A., 1892, 429), is best obtained by gently boiling a mixture of malonic acid, chloral, and acetic acid for several hours; a certain specimen of malonic acid, although apparently normal in all other respects, always failed to give this reaction. The substance can be distilled almost undecomposed in small quantities, b. p. 181—188°/17 mm.; methyl ester, rhombohedral crystals, m. p. 61—62°, b. p. 135—136°/13 mm.; *ethyl* ester, silky needles, m. p. 56—57°, b. p. 143—144°/12 mm.; the *acetyl* derivative, needles, m. p. 97—99°, gives an oily *methyl* ester, b. p. 130°/13 mm., D_4^{143} 1·3937, n_D^{145} 1·46815, and an oily *ethyl* ester, b. p. 134°/10 mm, D_4^{141} 1·3395, n_D^{141} 1·46458. All endeavours to produce a substance, $\underset{\mathrm{CH_2-CO}}{\mathrm{OH\cdot CH\cdot CCl_2}}{>}\mathrm{O}$, by elimination of hydrogen chloride from the tri-chlorohydroxybutyric acid were fruitless.

The method described by Kötz (A., 1907, i, 707) for the preparation of $\gamma\gamma\gamma$-trichlorocrotonic acid is found to yield the above trichloro-hydroxybutyric acid, and the m. p. given for the substance (*loc. cit.*) agrees with that of this acid. It is now found that the elements of water can be eliminated from trichlorohydroxybutyric acid by heating with acetic anhydride and sodium acetate; the resultant $\gamma\gamma\gamma$-*trichloro-crotonic acid* forms needles, m. p. 113—114°, b. p. 143—146°/18 mm.; it immediately reduces potassium permanganate in the cold, and is rapidly decomposed by hot water with formation of hydrochloric acid. The *potassium* and *silver* salts were prepared, the latter of which when heated in benzene on the water-bath eliminates silver chloride with the formation of a mixture of substances mainly complex, but possibly containing a little of the *lactone*, $\underset{\mathrm{CH-CO}}{\mathrm{CH-CCl_2}}{>}\mathrm{O}$. The acid forms an oily *methyl* ester, b. p. 85·4°/12 mm., D_4^{211} 1·3968, n_D^{211} 1·48075, and an oily *ethyl* ester, b. p. 100·5°/13 mm., D_4^{143} 1·3375, n_D^{143} 1·48693.

From the above results it follows that the group $-CCl_3$ exerts no special spectrochemical influence.   D. F. T.

The Constitution of the Chlorides of 1 : 2- and 1 : 3-Di-carboxylic Acids. KARL VON AUWERS and M. SCHMIDT (*Ber.*, 1913, 46, 457—487).—The consideration of the spectrochemical effect of chlorine in organic substances (von Auwers, A., 1912, ii, 1015) is extended to the question of the structure of such acid dichlorides

as succinyl and phthalyl chlorides (compare Scheiber, A., 1912, i, 559; Scheiber and Knothe, A., 1912, i, 701; Bredt, A., 1912, i, 411; Ott, A., 1912, i, 828). The decision of Bruhl as to the symmetrical structure of phthalyl chloride (*Ber.*, 1907, **40**, 884, 896) is based on too little experimental evidence to be entirely satisfactory; an investigation of the specific exaltations of the refractivity and dispersive power of various acid chlorides nevertheless indicates the correctness of this view.

A comparison of the chlorides and ethyl esters of crotonic, benzoic, and cinnamic acid shows that the exaltations in specific refractivity stand in the order acid > chloride > ester, whilst for the dispersion the exaltation is least for the ester, the free acid and the chloride being approximately equal. Phthalyl chloride shows no exceptional exaltation when compared with ethyl phthalate, the values in fact being in good agreement with those for the corresponding derivatives of benzoic acid; the results, however, when compared with those calculated for the unsymmetrical formula $C_6H_4{<}^{COCl_2}_{CO-}{>}O$ would indicate an improbably large exaltation.

The ethyl ester and chloride of fumaric acid exhibit exaltations approximately equal to those of the corresponding phthalic acid compounds; *iso*phthalic ester and chloride have exaltations appreciably higher, but this is probably to be attributed to the effects of structure isomerism. Maleyl chloride could not be obtained sufficiently pure for spectrochemical investigation.

In order to throw further light on this question, most of the chlorides of the oxalic series of acids were examined from oxalic to sebacic acid, and no exaltation was observed except a trace in the case of oxalyl chloride which may be attributed to the –CO·CO– group. Succinyl and glutaryl chloride must therefore be entirely of the symmetrical dichloride structure.

In the absence of pure, simple derivatives of the dichlorolactone molecule $^{CH·CCl_2}_{CH—CO}{>}O$, αδ dichloro-γ valerolactone,

$$^{CHCl·CO——}_{CH_2·CH(CH_2Cl)}{>}O$$
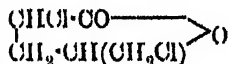
(Leuchs and Gius, A., 1912, i, 603, 604), was investigated and compared with the lactones of δ-methoxy- and δ-ethoxy-γ hydroxyvaleric acids, and with methyl αβ butyleneoxide-δ-carboxylate. All were found to be optically normal. It is therefore probable that the hypothetical dichlorolactonic structure for succinyl and phthalyl chlorides would also be optically normal.

d-*cis*-Camphoryl, *l*-*trans*-camphoryl, *d*-chlorocamphoryl, and dehydrocamphoryl chlorides from their spectrochemical behaviour are probably all normal acid chlorides. The first and third named certainly exhibit a certain negative exaltation, but as this is also to be observed with the corresponding esters it probably arises from the *gem*-dimethyl groups (see this vol., ii, 261).

A comparison of the chlorides and esters of chlorofumaric and fumaric acids shows a similar exaltation in the chloride and ester

of each acid, thus indicating the normal symmetrical structure of the chlorides. With chloromaleyl chloride, however, the molecular refraction is below that of the isomeric chlorofumaryl chloride, and is in agreement with that calculated on theoretical grounds for the structure

$$\begin{matrix} CH\cdot CCl_2 \\ \| \\ CCl-CO \end{matrix}\!>\!O$$; the lactonic formula is also favoured by a consideration

of the molecular volume (Ott, *loc. cit.*). The structure of phthalyl chloride, on the other hand, is almost certainly the symmetrical one, as is indicated by recent chemical and physicochemical investigations (Scheiber, *loc. cit.*; Ott, *loc. cit.*) and by the present confirmation of Brühl's results. The constitution of the chlorides of the isomeric camphoric acids, chlorocamphoric acid, and dehydrocamphoric acid is also decided in favour of the symmetrical acid chloride form (compare Scheiber and Knothe, *loc. cit.*).

Succinyl chloride gave curiously variable results for density, refraction, and dispersion, probably due to some difficultly removable impurity ; a specimen regarded as pure, indicated a true acid chloride structure, as already suggested by Ott.

The following substances were examined, but only the refraction for sodium light is quoted below; the original paper gives the values for the α-, β-, and γ-lines also.

Acetyl chloride, b. p. 51—52°, $D_4^{20\cdot6}$ 1·1039, $n_D^{20\cdot8}$ 1·38831 ; *isovaleryl* chloride, b. p. 114·5—115·5°/771 mm., $D_4^{21\cdot3}$ 0·9854, $n_D^{21\cdot3}$ 1·41361 ; crotonyl chloride, b. p. 117—120°/754 mm., $D_4^{17\cdot4}$ 1·0822, $n_D^{17\cdot9}$ 1·46001 ; methyl αβ-butyleneoxide-δ-carboxylate [γδ-oxidovalerate],
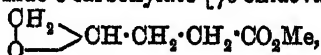
$$\begin{matrix} CH_2 \\ O \end{matrix}\!>\!CH\cdot CH_2\cdot CH_2\cdot CO_2Me,$$

$D_4^{24\cdot1}$ 1·0731, $n_D^{24\cdot7}$ 1·42589 ; δ-methoxy-γ-valerolactone, $D_4^{23\cdot6}$ 1·1205, $n_D^{23\cdot3}$ 1·44533 ; δ-ethoxy-γ-valerolactone, $D_4^{24\cdot5}$ 1·0718, $n_D^{24\cdot0}$ 1·44082 ; αδ - dichloro - γ - valerolactone, $D_4^{24\cdot2}$ 1·4367, $n_D^{?}$ 1·49624 ; oxalyl chloride, b. p. 60—61°, $D_4^{13\cdot4}$ 1·4884, $n_D^{13\cdot0}$ 1·43395 ; malonyl chloride, b. p. 58°/26 mm., $D_4^{23\cdot0}$ 1·4505, $n_D^{23\cdot1}$ 1·45973 ; succinyl chloride, b. p. 88·8°/19 mm , $D_4^{15\cdot3}$ 1·3948, $n_D^{15\cdot3}$ 1·47348 ; glutaryl chloride, b. p. 107—108°/16 mm., $D_4^{21\cdot8}$ 1·3221, $n_D^{20\cdot3}$ 1·47281 ; suberyl chloride, b. p. 149—150°/12 mm., $D_4^{20\cdot8}$ 1·1718, $n_D^{20\cdot6}$ 1·46847 ; sebacyl chloride, b. p. 168—170°/16 mm., $n_D^{18\cdot3}$ 1·46836 ; fumaryl chloride, b. p. 158—160°, $D_4^{16\cdot8}$ 1·4117, $n_D^{16\cdot1}$ 1·50038 ; chlorofumaryl chloride, b. p. 87—87·5°/28 mm., $D_4^{18\cdot3}$ 1·5653, $n_D^{17\cdot6}$ 1·52172 ; ethyl chlorofumarate, b. p. 135—136°/17 mm., $D_4^{14\cdot7}$ 1·1886, $n_D^{16\cdot1}$ 1·45782 ;

uns chloromaleyl chloride $\left(\begin{matrix} CH\cdot CCl_2 \\ \| \\ CCl-CO \end{matrix}\!>\!O,\ \text{Ott, } loc.\ cit.\right)$, b. p. 82·2—82·5°/ 26 mm , $D_4^{17\cdot7}$ 1·6055, $n_D^{18\cdot1}$ 1·51362.

Benzoyl chloride, $D_4^{20\cdot9}$ 1·2105, $n_D^{20\cdot9}$ 1·55376 ; cinnamoyl chloride, b. p. 131°/20 mm., $D_4^{43\cdot3}$ 1·1617, $n_D^{43\cdot5}$ 1·61364 ; phthalyl chloride, b. p. 156—157°/23 mm., $D_4^{15\cdot2}$ 1·4081, $n_D^{15\cdot5}$ 1·57099 ; ethyl phthalate, b. p. 162—163°/7 mm., $D_4^{17\cdot8}$ 1·1202, $n_D^{17\cdot7}$ 1·50293 ; *isophthalyl* chloride, m. p. 40—41°, $D_4^{47\cdot3}$ 1·3880, $n_D^{46\cdot9}$ 1·56999 ; ethyl *iso*phthalate, b. p. 170—170·5°/24 mm., $D_4^{16\cdot7}$ 1·1239, $n_D^{17\cdot5}$ 1·50815 ; *d-cis* camphoryl chloride, b. p. 144·5—145·5°/17 mm., $D_4^{20\cdot2}$ 1·2446, $n_D^{19\cdot9}$ 1·50133 ; ethyl *d-cis*-camphorate, b. p. 150—152°/8 mm., $D_4^{19\cdot2}$ 1·0318, $n_D^{19\cdot1}$ 1·45613 ;

l-trans-camphoryl chloride, b. p. 153—154°/24 mm , D_4^{30}" 1·2270, n_D^{207} 1·49880 ; ethyl *l-trans* camphorate, b. p. 155—157°/20 mm., D_4^{13} 1 0282, n_D^{11} " 1·45451 ; *d*-chlorocamphoryl chloride, b. p. 152—152·5°/ 17 mm., D_4^{15} 1·3219, n_D^{11} · 1·50797; *d* dehydrocamphoryl chloride, b. p. 160—161°/32 mm., D_4^{193} 1·2176, n_D^{45} 1 50433.　　　　D. F. T.

Preparation of Terpenylic and Terebic Acids　Rɛ́né Locquin

(*Bull. Soc. chim.*, 1913, [iv], **13**, 166—169).—Tiemann and his collaborators (A., 1895, i, 548 ; 1896, i, 385 ; 1897, i, 84) have suggested that methoethylheptanonolide yields terpenylic acid on oxidation by chromic acid, and terebic acid when oxidised by nitric acid, and may be used as a source of these two acids　The author finds that on oxidation by nitric acid, terpenylic acid is the chief product (58·2% of the theoretical), the yield of terebic acid (18 6% of the theoretical) being small.　The preparation and separation of the two acids are described.　　　　T. A. H.

Attempts to Synthesise Monosubstituted Paraconic Acids.

Philippe Barbier and Réné Locquin (*Bull. Soc. chim.*, 1913, [iv], **13**, 161—166.　Compare A., 1911, i, 708) —The only method hitherto available for the preparation of these acids is that of Fittig (A., 1890, i, 583), which gives poor yields when aliphatic aldehydes are used. The authors have modified Reformatsky's reaction for the production of β-hydroxy-acids (A., 1896, i, 128) with a view to preparing monosubstituted paraconic acids by this means, but the yields are poor, only 7% of the theoretical yield of *iso*propylparaconic acid being obtained, and 12% of the calculated yield of hexylparaconic acid.　The latter acid had m. p. 79—80°, which is 10° below that recorded by Schneegans.
　　　　T. A. H.

Preparation of Strontium Cholate.　Knoll & Co. (D.R.-P.

254530).—*Strontium cholate*, $(C_{24}H_{89}O_5)_2Sr,10H_2O$, colourless, hair-like tufts is readily obtained when an alcoholic solution of cholic acid is heated with an aqueous solution (or suspension) of strontium hydroxide ; it has an important therapeutic action.　　　　F. M. G. M.

Oxidation of Aldehydes by an Aqueous Solution of Bromine.

Ernest Anderson (*Amer. Chem. J.*, 1913, **49**, 179—184).—It is usually supposed that the method used for converting aldoses into the corresponding acids by oxidation with aqueous solution of bromine is not applicable to the ordinary aldehydes.　In order to test this question, several aldehydes have been subjected to the action of bromine, and the oxidation products isolated.　The results show that whilst benzaldehyde, acetaldehyde, paraldehyde, and formic acid give good yields of the corresponding acids, namely, benzoic, acetic, and carbonic, formaldehyde and aldol are oxidised to only a small extent, and salicylaldehyde and chloral not at all.

Acetaldehyde was found to give 71% of the theoretical yield of acetic acid ; benzaldehyde, 80% of benzoic acid ; paracetaldehyde, 86% of acetic acid ; and formic acid, 80% of carbonic acid.　　　　E. G.

Glyoxal. CARL D. HARRIES (*Ber.*, 1913, **46**, 294--296. Compare A., 1907, i, 183)—Polymerisation of glyoxal is accelerated by the presence of moisture. When technical glyoxal which has been dried over phosphoric oxide at 95° is distilled alone, the unimolecular compound is obtained. It is claimed that Meisenheimer's depolymerisation of methylglyoxal (A., 1912, i, 831) was foreshadowed in the above-mentioned paper.   J. C. W.

Catalytic Preparation of Ketones. JEAN B. SENDERENS (*Ann. Chim. Phys.*, 1913, [viii], **28**, 243—344).—A résumé of work already published (A., 1909, i, 286, 627; 1910, i, 11, 179, 489; 1911, i, 134, 302; 1912, i, 537).   H. W.

The Synthesis of Sugars by means of Radioactive Emanations. JULIUS STOKLASA, JOHANN ŠEBOR, and WENZEL ZDOBNICKÝ (*Compt. rend.*, 1913, **156**, 646—648. Compare A., 1911, i, 178, 769).—As with ultra-violet rays, so under the influence of radium emanation hydrogen and carbon dioxide react in the presence of potassium hydrogen carbonate, giving formaldehyde, which in the presence of potassium hydroxide polymerises and gives reducing sugars. No formates could be detected during the reaction. The sugars formed are a mixture of hexoses giving phenylosazones, separable into two fractions, one, m. p. 198—199°, and the other, m. p. 178°. Unlike the sugars obtained in the photochemical synthesis under the influence of ultra-violet rays (compare A., 1912, i, 606), these sugars are optically active and have $[\alpha]_D$ +17·58°. By distillation with hydrochloric acid indications of the presence of a pentose were obtained.
                                                W. G.

Preparation of δ-Dimethylamino-Δ^a-*iso*amylene and δ-Dimethylamino-Δ^a-butylene. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254529. Compare A., 1912, i, 742, 781; and Euler, A., 1897, i, 585).—δ-*Dimethylamino-Δ^a-isoamylene*,
                $CH_2{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}NMe_2$,
a colourless liquid, b. p. 113—116°, and identical with the so-called "β-methyldimethylpyrrolidine" (Euler, *loc. cit.*), can be prepared by heating γ-hydroxy-β-methylbutyldimethylamine with concentrated sulphuric acid (3 parts) during three to four hours at 100°, or with 50% sulphuric acid (5—10 parts) during ten hours at 150—160°.
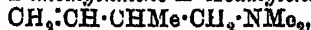
δ-*Dimethylamino-Δ^a-butylene*, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$, a colourless liquid, b. p. 94—96°, is obtained in a similar manner from γ-hydroxybutyldimethylamine with 20—30% sulphuric acid (5 parts) at 200° during ten hours.

These compounds have an odour of goniine, and find employment in the preparation of isoprene and erythene.   F. M. G. M.

Preparation of δ-Dimethylamino-γ-dimethylbutan-β-ol. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254713).—When methyl tetramethyldiamino*iso*propyl ketone (following abstract) is boiled during one hour with 20% sulphuric acid (4—6 parts), it furnishes *dimethylamino-β-acetylallylene*, $CH_2{:}CAc{\cdot}CH_2{\cdot}NMe_2$, which

on reduction gives rise to δ-dimethylamino-γ methylbutan-β-ol (A., 1911, i, 598), a colourless oil, b. p. 67—69°/17 mm.   F. M. G. M.

Preparation of Amino- and Diamino-ketones of the Aliphatic Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 254714. Compare A., 1911, i, 598, and preceding abstract). —When dimethylaminomethyl alcohol, $OH \cdot CH_2 \cdot NMe_2$, or tetramethyldiaminomethane, $Me_2N \cdot CH_2 \cdot NMe_2$, are condensed with acetone (or its homologues), the following reactions take place (R = hydrogen or alkyl).

1. $CH_3 \cdot CO \cdot CH_2R + OH \cdot CH_2 \cdot NMe_2 =$
$$CH_3 \cdot CO \cdot CHR \cdot CH_2 \cdot NMe_2 + H_2O.$$

2. $CH_3 \cdot CO \cdot CH_2R + NMe_2 \cdot CH_2 \cdot NMe_2 =$
$$NHMe_2 + CH_3 \cdot CO \cdot CHR \cdot CH_2 \cdot NMe_2.$$
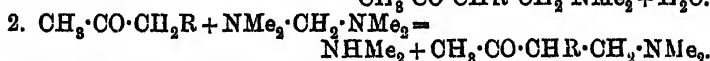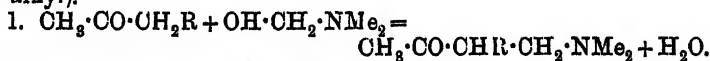
The following compounds are described : dimethyl-β-acetylpropyl-amine (*loc. cit.*), b. p. 51—51·5°/13 mm.

ββ-Acetylmethyltrimethylenetetramethyldiamine [*methyl tetramethyldiaminotert.-butyl ketone*], $CH_3 \cdot CO \cdot CMe(CH_2 \cdot NMe_2)_2$, a colourless, viscous oil, b. p. 110—112°/18 mm., from methyl ethyl ketone and dimethylaminomethyl alcohol.

β-Acetylethyldimethylamine [*methyl dimethylaminoethyl ketone*],
$$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot NMe_2,$$
a colourless oil with a strong ammoniacal odour, b. p. 57—58°/18 mm. ; and *β-acetyltrimethylenetetramethyldiamine* [*methyl tetramethyldiamino-*iso*propyl ketone*], $CH_3 \cdot CO \cdot CH(CH_2 \cdot NMe_2)_2$, a colourless, odourless, viscous oil, b p. 96—98°/16 mm.
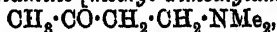
These compounds are employed in the preparation of erythrene and isoprene.   F. M. G. M.

Preparation of Urethanes of Tertiary Alcohols. EMANUEL MERCK (D.R.-P. 254472. Compare this vol., i, 5).—It is found that the halogen formyl esters described previously can be readily converted by the action of ammonia or substituted ammonias into urethanes of tertiary alcohols :
$$OR \cdot CO \cdot Cl + 2NHR_1R_2 \longrightarrow OR \cdot CO \cdot NR_1R_2 + NHR_1R_2, HCl,$$
where RO is a tertiary alcoholic group, and R_1 and R_2 hydrogen, alkyl or aryl groups.

Dimethylethylcarbinyl chloro-formate with alcoholic ammonia furnishes a *urethane*, colourless needles, m. p. 85—87° ; an *ethyl urethane*, a colourless oil, b. p. 89°/13 mm., and 86°/11 mm. ; a *phenyl-urethane*, colourless crystals, m. p. 44—47°, b. p. 146°/9 mm. ; a *methyl-phenylurethane*, a colourless oil, b. p. 133°/13 mm., and with *p*-pheno-tidine a p-*ethoxyphenylurethane*, colourless needles, m. p. 88—90°, whilst methyldiethylcarbinol gives rise to a *urethane*, colourless needles, m. p. 61°, and a *phenylurethane*.   F. M. G. M.

Behaviour of Formamide Under the Influence of the Silent Electric Discharge. The Question of Nitrogen Assimilation. WALTHER LÖB (*Ber.*, 1913, **46**, 684—697).—In the course of some experiments on the influence of the silent electric discharge on various combinations of moist carbon dioxide, carbon monoxide,

alcohol and ammonia, with or without oxygen or air, the only com
pound obtained which could be regarded as of interest to the problem
of nitrogen assimilation was hexamethylenetetramine (A , 1909, i, 769).
Further investigations on the behaviour of this compound towards
oxidising and reducing agents, and towards living yeast, showed that
it had no relation to the amino-acids, and, therefore, throws no light
on the general question. The discovery of Losanitsch and Jovitschitsch
(A., 1897, i, 179) that ammonia and carbon monoxide produce form-
amide led the author to regard this compound as an intermediate stage,
and to try the effect of the silent discharge on the dry substance and
on an aqueous solution, both boiling under reduced pressure.   In the
former case, oxamide was deposited on the sides of the discharge tube,
and in the latter, as would be expected, ammonium oxamate. Some
reduction was therefore necessary in order to arrive at glycine.
Previous experience had shown that water itself is a reducing agent
under these conditions (A., 1906, ii, 324), whilst the reaction
$CO + H_2O = CO_2 + H_2$ had also to be considered. The resolution of
some formamide into carbon monoxide and ammonia was to be
expected, and, indeed, an examination of the gases liberated during the
experiment proved the presence of these substances.   The existence
of glycine in the product, after the removal of ammonia, was unques-
tionably demonstrated by the formaldehyde test of Sörensen, the
"deaminising" method of van Slyke, the reaction with triketo-
hydrindene hydrate, and the formation of the naphthalenesulphonyl
compound (E. Fischer and Bergell, A., 1903, i, 24).

The presence of glycine could also be observed on repeating the
experiment with moist carbon monoxide and ammonia. The formation
of glycine from carbon dioxide (which breaks down into carbon
monoxide under the influence of the silent discharge), ammonia, and
water is therefore a process of reduction, and the oxidation of glycine
should lead to these or intermediate products. Halsey has shown
that the products of the action of permanganate do, indeed, include
formamide and oxamic acid (A , 1898, ii, 529).

The reactions may be formulated thus:
$$\text{(I)} \quad 2CO_2 + 2NH_3 + H_2O \longrightarrow 2H \cdot CO \cdot NH_2 + H_2O + O_2.$$
$$\text{(II)} \quad 2H \cdot CO \cdot NH_2 + H_2O \longrightarrow NH_2 \cdot CO \cdot COONH_4 + H_2.$$
$$\downarrow$$
$$NH_2 \cdot CH_2 \cdot COONH_4 + O.$$
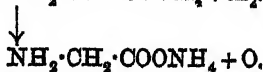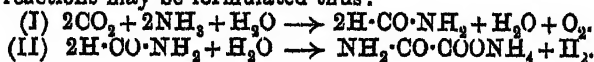
Reference must be made to the original paper for the experimental
details, but it may be said that the amount of oxamide accumulated
during twenty hours from 20 grams of dry formamide, boiling at
110°/15 mm., was about 0 05—0·08 gram, whilst about 0·01 gram of
ammonium oxamate was obtained from a 5 –10% solution during the
same time, the glycine present being comparable with a 0 01% solution.
                                                                J. C. W.

The Diamide of Sulphoisobutyric Acid. JACOB MOLL VAN
CHARANTE (Rec. trav. chim., 1913, 32, 90—96. Compare A., 1905, i,
16).—Sulphoisobutyrodiamide, $NH_2 \cdot SO_2 \cdot CMe_2 \cdot CO \cdot NH_2$, was obtained
by passing ammonia into a cold methyl-alcoholic solution of methyl

chlorosulpho*iso*butyrate. It decomposed without melting at about 340°. At 17°, one part of diamide dissolved in 201·8 parts of water, whilst at 100° the solubility was one part in 24·9. It was insoluble in the other usual solvents. Attempts to condense it with carbonyl chloride, in the presence or absence of a catalyst, were unsuccessful. Similarly, oxalyl chloride, alone or in benzene solution, was without action on it.

To determine whether it was possible to cause a sulphonamide to react with oxalyl chloride, a solution of benzenesulphonamide and oxalyl chloride in benzene was boiled during two and a-half days. Hydrogen chloride was slowly evolved, and *diphenylsulphonoxamide*, $C_2O_2(NH·SO_2Ph)_2$, formed. It had m. p. 256° (corr., slight decomp.).

H. W.

Extraction of Glutamic Acid Hydrochloride and Betaine Hydrochloride from Molasses Residue. HUGO STOLTZENBERG (*Ber.*, 1913, **46**, 557—566. Compare A., 1912, i, 680).—Molasses residue is mixed with hydrochloric acid and subsequently saturated with hydrogen chloride. The crude hydrochlorides which are precipitated are treated with alcohol and hydrogen chloride, whereby glutamic acid hydrochloride is converted into the readily soluble ester hydrochloride. The solution of the latter is concentrated to a syrup, the residue boiled with water, the solution filtered from humin, decolorised, and concentrated until crystallisation begins, when it is again saturated with hydrogen chloride, whereby glutamic acid hydrochloride is precipitated. This has m. p. 213° when rapidly heated, and is shown to be partly racemised, the highest observed value for $[\alpha]_D^{15}$ being $+26·15°$ in 10% hydrochloric acid solution, whereas Siegfried and Schutt (A., 1912, i, 952) observed $+34·89°$. Purification by transformation into the barium salt and subsequent reprecipitation of the hydrochloride effected no improvement. The filtrates obtained after removal of glutamic acid hydrochloride deposited, on evaporation, betaine hydrochloride, and contained also a strongly acid *substance*, which could not be obtained in the crystalline state.

The remainder of the paper consists of a reply to the criticisms brought by Ehrlich (A., 1912, i, 835) against the previous work of the author (*loc. cit.*). Stoltzenberg's process of isolating betaine hydrochloride from molasses differs essentially from that of Ehrlich (1904, D.R.-P. 157173), in that hydrochloric acid and alcohol are employed in the given order in the former process, in the inverse order in the latter. In the second method, the chemical nature of the residue is not affected by agitation with alcohol, and the hydrogen chloride is only used to precipitate the hygroscopic betaine. In the first method, however, the composition of the residue itself is greatly altered by the action of the hydrogen chloride. Ehrlich's statement that the alcohol consumption is less in his process than in that of the author is incorrect.

The paper concludes with a critical survey of the historical development of the subject as described by Ehrlich. H. W.

Action of Sodium Hypobromite on Semicarbazide. ROBERT STOLLÉ (*Ber.*, 1913, **46**, 260. Compare Linch, T., 1912, **101**, 1755).

—The product of the action of sodium hypobromite on semicarbazide is hydrazodicarbonamide, and not *p*-urazine as described by Linch. The compound obtained on oxidation with chromic acid is therefore azodicarbonamide (Thiele, A., 1892, 1295 and 1430), and not a stable tetrazine.   J. C. W.

Salt- and Complex Salt-Formation with Amino- and Hydroxy-acetohydroxamic Acids. HEINRICH LEY and F. MANNCHEN (*Ber.*, 1913, **46**, 751—758).—On account of the similarity in structure between the carboxylic and hydroxamic acids, the authors have investigated certain derivatives of the latter in which the formation of complex salts was to be expected. It is found that internally complex salts are obtainable from amino- and hydroxy-hydroxamic acids somewhat analogous to those obtained from the simple amino-acids. To the normal copper salts is attributed the

structure $R{\cdot}C{<}^{NO}_{O}{>}Cu$; acid salts could be obtained only from sub-

stituted hydroxamic acids, and the constitution suggested is

$$CH_2{<}^{NH_2}_{C(:NOH){\cdot}O}{>}M{<}^{NH_2}_{O{\cdot}C(:NOH)}{>}CH_2$$
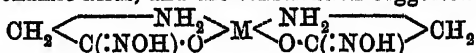
(compare Ley, A., 1909, i, 138), where M represents a bivalent metal atom. Complex salts containing a bivalent metal together with an alkali metal could be obtained both from the unsubstituted and substituted acids ; the heavy metal is present as part of a complex ion, but from the colour of the salts of the amino- and hydroxy-substituted acids the conclusion is drawn that this atom is also linked with the anion complex by supplementary partial valencies.

Aminoacetohydroxamic acid, $NH_2{\cdot}CH_2{\cdot}C(OH){:}N{\cdot}OH$, was obtained by the interaction of equimolecular quantities of hydroxylamine, ethyl aminoacetate, and sodium ethoxide in alcoholic solution ; it was precipitated as the copper salt and recovered by the action of hydrogen sulphide ; it is a colourless, crystalline solid, m. p. 107° (approx.) ; normal *copper* salt, green, amorphous powder, obtained by mixing aqueous solutions of the acid and copper acetate ; *acid copper* salt, obtained by adding copper acetate to a solution of the *sodium* salt, separates in violet crystals ; *acid nickel* salt, prepared by the addition of dilute sodium hydroxide solution to a solution of nickel acetate with a bimolecular quantity of the acid, forms deep red crystals ; the complex *sodium nickel* salt, $(C_2H_3O_2N_2)_2NiNaH,H_2O$, yellowish-red, rhombic tablets, was obtained by treating a solution of the sodium salt with nickel acetate and sodium hydroxide.

Anilinoacetohydroxamic acid, $NHPh{\cdot}CH_2{\cdot}C(OH){:}N{\cdot}OH$, colourless needles, m. p. 126° (decomp.), separates in the form of the *sodium* salt when ethyl anilinoacetate is treated in alcoholic solution with an equimolecular quantity of hydroxylamine ; *copper* salt, green, amorphous solid.

Phenylglycollohydroxamic acid, $OH{\cdot}CHPh{\cdot}C(OH){:}N{\cdot}OH$, colourless, rhombic leaflets, m. p. 132°, was prepared in a similar manner to the last ; *sodium* salt, needles ; the green *copper* salt, like that of the last acid, gives a violet solution in aqueous sodium hydroxide ; the *nickel sodium* salt could be obtained only as a reddish-yellow solution.

The free acid soon decomposes in solution with the formation of benzaldehyde.

Phenoxyacetohydroxamic acid, $OPh \cdot CH_2 \cdot C(OH){:}N \cdot OH$, prepared in an analogous manner from ethyl phenoxyacetate, forms colourless leaves, m. p. 114°; the addition of copper acetate and sodium hydroxide solution to the solution of the *sodium* salt causes the formation of the crystalline, bluish-violet *copper sodium* salt,

$$(C_8H_7O_3N)_2CuNa_2, 2H_2O,$$
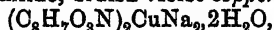
which is converted by water into the green *copper* salt.

The interaction of equimolecular quantities of hydroxylamine, ethyl lactate, and sodium ethoxide in alcoholic solution produces unstable *sodium lactohydroxamate*, $CH_3 \cdot CH(OH) \cdot C(ONa){:}NOH$.

An aqueous solution of acetohydroxamic acid (Miolati, A., 1892, 699) when treated with copper acetate and sodium hydroxide, after some days, deposits blue crystals of a complex *copper sodium* salt,

$$(C_2H_3O_2N)_2CuNa_2, 7H_2O,$$
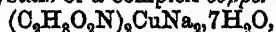
which is converted by water into the ordinary green copper salt.

<div align="right">D. F. T.</div>

New Method of Preparing Nitriles of the Aliphatic Series. ALEXANDER E. ARBUZOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 74—79). —Catalytic decomposition of the hydrazones of aliphatic aldehydes in presence of cuprous chloride, platinous chloride, or zinc chloride always yields nitriles to some extent, although the yield varies considerably. In general, hydrazones containing small radicles give very small proportions of nitriles, the decomposition then yielding principally substituted indoles and other compounds (see this vol., i, 388). On the other hand, hydrazones containing large radicles, such as *iso*valeraldehydephenylhydrazone, undergo nitrilic decomposition almost exclusively : $C_5H_{10}N \cdot NHPh = NH_2Ph + C_5H_9N$.

*iso*Valeronitrile, thus obtained in 56% yield, is a colourless, mobile liquid, b. p. 128·5°, or 52·5—53°/50 mm., D_0^0 0·7884, D_0^{20} 0·8054 (compare Erlenmeyer, *Annalen*, 1871, **160**, 266).

*iso*Butyronitrile is similarly obtained from *iso*butaldehydephenylhydrazone in 37% yield, and *n*-heptonitrile, b. p. 183·5°, D_0^{20} 0 8107 (compare Henry, A., 1905, i, 561), from *n*-heptaldehydephenylhydrazone.

<div align="right">T. H. P.</div>

Chromates and Mercuric Cyanide. DANIEL STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1913, **80**, 155—160. Compare A., 1912, ii, 648).—The following compounds have been obtained :

$$(NH_4)_6Cr_2O_7Cl_4, 6Hg(CN)_2, 4H_2O,$$
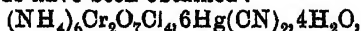
long, reddish-yellow crystals, with only a narrow range of stability ; $2K_2CrO_4, 3Hg(CN)_2, 2H_2O$. A chloride-chromate salt has not been obtained in the case of potassium.

<div align="right">C. H. D.</div>

Potassium β-Ferricyanide. HORACE L. WELLS (*Amer. Chem. J.*, 1913, **49**, 205—206).—Hauser and Biesalski (this vol., i, 26) have stated that the potassium β-ferricyanide described by Locke and Edwards (A., 1899, i, 407) is merely the ordinary salt, contaminated with colloidal Prussian-blue. It is now shown that this view is incorrect, and that Hauser and Biesalski have overlooked the fact that the

β ferricyanide does not yield a precipitate with bismuth nitrate, and is thus readily distinguished from the ordinary salt.   E. G.

Crystalline Form of Two Scandium Platinocyanides. PETR N. TSCHIRVINSKI (*Zeitsch. Kryst. Min.*, 1913, **52**, 44—47).—The crystalline form, as observed under the microscope, is described for the yellow salt, $Sc_2[Pt(CN)_4]_3,18H_2O$, and for the red salt,
$$Sc_2[Pt(CN)_4]_3.21H_2O.$$
New observations are also given for the yttrium salt,
$$Y_2[Pt(CN)_4]_3,21H_2O.$$ L. J. S.
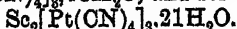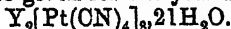
Magnesium Methyl Iodide. PIERRE JOLIBOIS (*Compt. rend.*, 1913, **156**, 712—714. Compare A., 1912, i, 675, 753).—The action of methyl iodide on magnesium in dry ether is a simple one, there being practically no secondary reaction under any conditions. The magnesium methyl iodide, so obtained, when heated in a vacuum, first loses its ether of constitution at 130°, and at 240° methane is evolved, according to the equation : $2MgMe_2,MgI_2 = 3CH_4 + Mg_2C,2MgI_2$.

By raising the temperature to 600° no more gas is evolved. The residue is a voluminous, yellow mass, from which only a definite portion of the iodine can be extracted in the form of magnesium iodide by dry ether, leaving a *compound*, having the definite composition Mg_2C,MgI_2, which is violently decomposed by water with development of light and heat, and, on controlled decomposition by moist ether, yields practically pure methane.   W. O.

The Catalytic Hydrogenation of Camphorone. Some New *cyclo*Pentane **Hydrocarbons.** MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1913, **156**, 470—473).—Camphorone on hydrogenation in the presence of reduced nickel at 130° yields dihydrocamphorone (compare Semmler, A., 1904, i, 260). If the reduction is carried out at 280°, the product obtained is 1-*methyl*-3-*iso*-*propyl*cyclopentane, $C_5H_8MePr^\beta$, a liquid with a terpene-like odour, b. p. 132—134°, D^{19} 0·773, n_D^{19} 1·4250. The same compound is obtained by dehydrating 1-methyl-3-*iso*propyl*cyclo*pentane-2-ol with zinc chloride, which furnishes a mixture of two isomeric unsaturated hydrocarbons, b. p. 143—145°, D^{18} 0·786, n_D^{18} 1·4465, non-separable, but which on hydrogenation at 170° are converted into the pentane hydrocarbon.

Dihydrocamphorone reacts with magnesium methyl iodide, giving a mixture of 1 : 2-*dimethyl*-3-isopropyl-Δ^1- and -Δ^2-*cyclopentenes*, b. p. 150—155°, D^{17} 0·812, n_D^{17} 1·4500, which on hydrogenation at 180° are transformed into 1 : 2-*dimethyl*-3-isopropyl*cyclo*pentane, b. p. 146—148°, D^{16} 0·786, n_D^{16} 1·4337. Similarly by using magnesium *iso*propyl iodide a mixture of 1-*dimethyl*-2 : 3-*diisopropyl*-Δ^1- and -Δ^2-*cyclopentene*, b. p. 160—168°, D^{16} 0·812, n_D^{18} 1·4509, is obtained, yielding on hydrogenation at 180°, 1-*methyl*-2 : 3-*diisopropyl*cyclopentane, b. p. 150—152°, D^{17} 0·781, n_D^{17} 1·4318.   W. G.

The *cyclo*Octane **Series. VI.** *cyclo*Octatetraene. RICHARD WILLSTÄTTER and MICHAEL HEIDELBERGER (*Ber.*, 1913, **46**, 517—527. Compare Willstätter and Waser, A., 1912, i, 17).—The previous

observations with *cyclo*octatetraene have been repeated and extended. The quaternary ammonium base is now distilled in a still lower vacuum and at a correspondingly lower temperature (30—45°). On cooling, the hydrocarbon solidifies to a pale yellow, crystalline mass, m. p. − 27°. It forms an additive compound with bromine, taking up two atoms only. The *dibromide*, $C_8H_8Br_2$, crystallises in lustrous, snow-white needles, m. p. 70—71·5° (corr.). It decolorises permanganate instantaneously and tends to take up more bromine, but hydrogen bromide is then eliminated, and a *substance*, $C_8H_7Br_3$, m. p. 53—55°, is obtained instead of the tetrabromide.

The tetraene reacts immediately with chlorine, and hydrogen chloride is eliminated ; an oily *chloride* is obtained, and can be separated into two fractions, both of which have the composition $C_8H_7Cl_3$.

With hydrogen bromide in acetic acid solution the tetraene forms a *hydrobromide*, C_8H_9Br, which is an almost colourless oil with a sweet odour, b. p. 85—87°/12·5 mm. It slowly decomposes in presence of oxygen, and gives an orange coloration with concentrated sulphuric acid.

The molecular refraction of *cyclo*octatetraene shows little or no exaltation. Similarly, the molecular dispersion $(\beta—\alpha)$ shows no marked exaltation, although in consequence of the greater dispersion in the ultra-violet the molecular dispersion, $M_\gamma—M_\alpha$, shows a larger exaltation.

The tetraene behaves, like benzene, optically normal in regions where it is free from absorption ; the dispersion is, however, abnormal in the region where selective absorption takes place.

Such selective exaltation of the molecular dispersion is even more marked in the case of the yellow fulvenes ; data are quoted for methylethylfulvene and dimethylfulvene, as well as *cyclo*octatriene.

When *cyclo*octatetraene is hydrogenated by the platinum method the yellow colour disappears after the addition of 1·5 molecules of hydrogen. The first three molecules appeared to be absorbed in approximately equal times and the fourth more slowly, the actual figures being 35, 40, 40, and 95 minutes respectively.

Methylethylfulvene does not lose the yellow colour until reduction is nearly complete. The three molecules of hydrogen were absorbed in 7, 7, and 10 minutes.

The product, *sec.-butyl*cyclopentane, is a mobile liquid, with an odour like limonene, b. p. 152—154°/725 mm., D_4^0 0·810.

The *cyclo*octane formed even from pure *cyclo*octatetraene is not pure, and probably contains an isomeride.

Pure *cyclo*octatetraene may be kept for several months without decomposition. E. F. A.

[Preparation of *cyclo*Hexene.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 254473. Compare A., 1899, i, 22 ; 1902, i, 2, and T., 1898, 73, 941).—When the vapour of chloro*cyclo*hexane at 350—450°/15—20 mm. is conducted over a catalytic agent (such as barium chloride, aluminium oxide, or nickel chloride), it gives rise to. *cyclo*hexene. F. M. G. M.

Rational Preparation of Some Benzene Homologues.   II.
FRANZ KUNCKELL and GEORG ULEX (*J. pr. Chem.*, 1913, [ii], **87**,
227—236).—A continuation of previous work (this vol., i, 29) on the
preparation of benzene homologues by the interaction of alkyl esters of
chloro-formic acid with aromatic hydrocarbons in the presence of
aluminium chloride.

Methyl chloro-formate reacts with benzene to form toluene and
m-xylene; with toluene it yields *p*-xylene and ψ-cumene.

The interaction of ethyl chloro-formate with benzene and toluene
yields respectively *p*-diethylbenzene and 1-*methyl*-3 : 4-*diethylbenzene*,
b. p. 200—203°, the constitution of which has been established by its
oxidation to 4-methylphthalic acid.

m-Xylene reacts with ethyl chloro-formate, yielding 1 : 3-*dimethyl*-
5-*ethylbenzene*, b. p. 182—188°, and with *p*-xylene to form 1 : 4-*dimethyl*-
2-*ethylbenzene*, b. p. 183—185°.

The interaction of cumene with methyl and ethyl carbonates yields
dimethylisopropylbenzene, b. p. 195—210°, and *diethylisopropylbenzene*,
b. p. 250—256° respectively.

The addition of *iso*butyl chloro-formate to a mixture of aluminium
chloride and benzene gives rise to *tert.*-butylbenzene, whilst the
addition of aluminium chloride to a mixture of the ester with
benzene yields *di*-(tert. ?)-*butylbenzene*, b. p. 225—235°, and *tri*-(tert. ?)-
butylbenzene.

The preparation of a *p*(?)-methylbutylbenzene, b. p. 190—195°, and a
methyldibutylbenzene, b. p. 241—247°, from toluene and *iso*butyl chloro-
formate, and p-*methylamylbenzene*, b. p. 205—210°, from amyl chloro-
formate and toluene is also described.   F. B.

Chemical Action of Light.   XXV.   Autoxidations.   III.
GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1913, **46**, 417—422*).—
A continuation of the investigation of the autoxidation of aromatic
hydrocarbons (A., 1912, i, 174, 645)   The results are in accordance
with those of Suida (A., 1912, i, 957), but as the present authors gave
prolonged exposure to light and investigated only the final products,
indications of peroxides were but rarely observed.

Benzene in contact with water and oxygen is completely unaltered
after several months' exposure to sunlight (compare Suida, *loc. cit.*).

Ethylbenzene under similar conditions gives a yellow aqueous layer,
and after neutralisation with sodium carbonate, ether extracts aceto-
phenone with some unchanged ethylbenzene ; the former was charac-
terised by its semicarbazone; this, it was observed, separates from
methyl alcohol with one molecule of alcohol of crystallisation, which is
lost on drying over sulphuric acid.   The alkaline solution, which
had been extracted with ether, was found to contain formic and benzoic
acids.

Mesitylene, when treated similarly, gave a strongly acidic mixture,
which after neutralisation yielded an ethereal extract containing
mainly unchanged hydrocarbon, together with a small quantity of a
non-volatile *substance* and a trace of an aldehyde.   The aqueous liquid
on acidification gave formic acid, mesitylenic acid, a substance probably

a polycarboxylic acid which sublimed near 300°, and some resinous matter.

The oxidation product of ψ-cumene contained as its neutral constituents only unchanged hydrocarbon and a trace of an aldehydic substance ; the acidic constituents comprised formic acid, together with 3 : 4-dimethylbenzoic acid, 2 : 4-dimethylbenzoic acid, and a difficultly volatile, crystalline *substance* ; the presence of 2 : 5-dimethylbenzoic acid could not be detected.

Indene was practically completely changed, and the reaction mixture slowly gave the reaction for a peroxide. A relatively large amount of resinous matter was produced which was partly soluble in ether, the soluble portion being separable by boiling water into a colourless *substance*, crystallising in leaflets, m. p. 72°, and a yellow, amorphous substance, m. p. 123° (approx.). The acidic portion of the reaction product contained formic and phthalic acids, together with a third substance, m. p. 174°, probably homophthalic acid.

Naphthalene proved quite resistant to autoxidation, but tetrahydronaphthalene (Bamberger and Kitschelt, A., 1890, 1146) is readily oxidised, giving much resinous matter and a little phthalic acid.

D. F. T.

Influence of Substituents in Benzene on the Binary Systems. Substituted Benzene–Antimony Trihaloids. BORIS N. MENSCHUTKIN (*J. Chim. phys.*, 1912, 10, 598—611. Compare A., 1912, i, 98, 99, 100, 177).—The compounds of benzene with antimony trichloride and tribromide are of the type $2SbCl_3,C_6H_6$, but some substituted benzenes give in addition compounds of the type $SbCl_3,PhR$. Methyl-, ethyl-, propyl- and *iso*amyl-benzenes exhibit a decreasing stability in the compounds $2SbCl_3,PhR$, whereas the stability of the compounds $SbCl_3,PhR$ attains a maximum in ethylbenzene.

Antimony tribromide has less affinity for the phenyl nucleus than the chloride. Toluene gives compounds of both types, but ethyl-, propyl- and *iso*amyl-benzenes of the type $SbBr_3,PhR$ only, the ethyl compound again having the maximum stability.

Diphenyl forms the compounds $2SbCl_3,PhPh$ (stable) and
$$2SbBr_3,PhPh$$
(unstable), and diphenylmethane gives two stable compounds of the same types. Triphenylmethane, however, does not combine with antimony tribromide, and with the chloride gives only an unstable compound of the formula $SbCl_3,CHPh_3$.

The xylenes form with antimony trichloride compounds of both types, which are intermediate in stability between those of toluene and ethylbenzene. *p*-Xylene gives the most, and *m*-xylene the least, stable. With antimony tribromide, *p*-xylene gives only the compound $2SbBr_3,C_6H_4Me_2$, which is intermediate in stability between those of benzene and toluene, whilst *m*- and *o*-xylene give also compounds, $SbBr_3,C_6H_4Me_2$, which are less stable than that of toluene.

The compounds of antimony trichloride and tribromide with cymene are analogous in composition and inferior in stability to those of *p*-xylene. The unfavourable influence of the *iso*propyl group is thus manifest in presence of the methyl group.

Mesitylene and ψ-cumene form compounds of both types with antimony trihaloids, those of ψ-cumene being less and those of mesitylene more stable than the toluene compounds. Apparently the three methyl groups in mesitylene neutralise each other's effects on the phenyl nucleus.   R. J. C.

Influence of Substituents in Benzene on the Properties of the Binary Systems Formed by Substituted Benzenes and Antimony Trichloride or Tribromide. BORIS N. MENSCHUTKIN (*J. Chim. phys.*, 1912, **10**, 612—623. Compare A., 1912, i, 193).— The compounds of monosubstituted benzenes with antimony trichloride are all of the two types $2SbCl_3,PhR$ and $SbCl_3,PhR$. When R is H, OH, Me, OMe, Et, Pr^a or $C_5H_{11}^{\beta}$, both compounds are formed. When R is OEt, Bz, Ph, COH, COMe, COPh, CN, compounds of the second type only are produced. When R is NO_2, F, Cl, Br, I, CHPh$_2$, compounds of the second type are also produced, which, however, decompose on melting, and when R is SO_3H, CO_2H, or COCl no combination occurs.

From the behaviour of phenol and anisole it is argued that oxygen has very little influence, although in phenetole the cumulative effect of the oxygen and the ethyl group prevents the formation of the compound $2SbCl_3,PhOEt$. Neither anisole nor ethylbenzene forms compounds of this type with antimony tribromide. Nitro-, fluoro-, chloro-, bromo-, and iodo-benzene do not combine with the tribromide at all.

m-Dinitrobenzene gives an unstable compound, $SbCl_3,C_6H_4(NO_2)_2$, which, like the compound $SbCl_3,PhI$, does not invariably crystallise out, so that complete f.p. diagrams of these systems are obtainable showing only one eutectic point. The nitro-group diminishes the affinity of the phenyl nucleus for antimony less than the halogens. *p*-Dichloro- and *p*-dibromo-benzene do not combine with antimony trichloride.

p-Chlorotoluene gives no compounds, but *o*- and *m*-chlorotoluene give compounds, $SbCl_3,C_6H_4MeCl$, which decompose on melting. No corresponding compounds of antimony tribromide exist.

The three nitrotoluenes form compounds of the formula

$$SbCl_3,C_6H_4Me\cdot NO_2,$$
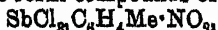
the most stable being given by *o*-nitrotoluene, which also combines with antimony tribromide.

Benzene has more affinity for antimony haloids than any of its derivatives, but *cyclo*hexane does not combine at all. The degree of saturation of the phenyl nucleus varies with the nature of the substituting atoms or groups. This variation is not expressible by ordinary structural formulæ, but such formulæ as have been proposed recently by Kaufmann and by Stark are capable of giving some explanation of it.

The compounds of aniline containing 1, 2, 3, 4, and 6 molecules of aniline per molecule of antimony trichloride are in a class by themselves, and are to be attributed to the residual affinity of the amino-group.   R. J. C.

The Catalytic Action of Mercury in Nitrations. RICHARD WOLFFENSTEIN and OSKAR BOTERS (*Ber.*, 1913, 46, 586—589).— Mercury has no catalytic action on the nitration of benzene when concentrated nitric acid or a nitric acid-sulphuric acid mixture is used, nitrobenzene being formed as usual (compare Holdermann, A., 1906, i, 439). When, however, a more dilute nitric acid (D = 1·31) is used, nitro-phenols are produced. The reaction is first one of oxidation to phenol, and then nitration, since when nitrobenzene is used instead of benzene, no trace of a nitrophenol is produced. Similar reactions take place with toluene, and ethyl- and propyl-benzenes.

To prepare dinitro- or trinitro-phenol, a mixture of benzene (100 grams), nitric acid (800 grams; D = 1·31), and mercuric nitrate (15 grams) is heated on the water-bath under reflux, stirring vigorously meanwhile. At the end of the reaction, the flask contains a mass of crystals of 2 : 4-dinitrophenol and of picric acid. Additive mercury compounds are formed as intermediate products.

Instead of using nitric acid, nitrous acid, nitrogen dioxide or tetroxide, and nitrogen pentoxide may be used. For example, a mixture of 120 grams of benzene, 20 grams of mercuric nitrate, and 270 grams of nitrogen tetroxide is kept at the ordinary temperature for a few days, after which a crystalline mass of almost pure 2 : 4-dinitrophenol is obtained. T. S. P.

Hydrogenation of Aromatic Compounds by means of Platinum and Hydrogen. II. Dihydronaphthalene. RICHARD WILLSTÄTTER and VICTOR L. KING (*Ber.*, 1913, 46, 527—535. Compare Willstätter and Hatt, A., 1912, i, 545).—Dihydronaphthalene has not previously been prepared free from contamination with naphthalene or tetrahydronaphthalene. It may be obtained pure by distilling the quaternary hydroxide of tetrahydro-β-naphthylamine in a vacuum, or more conveniently by reducing naphthalene dibromide by means of zinc powder and alcohol at 60°. Pure dihydronaphthalene is a colourless oil with a sweet odour, b. p. 84·5°/16 mm., D_1^{20} 0·9974 ; it crystallises in large plates, m. p. − 9°.

When hydrogenated by means of platinum and hydrogen, the first stage is the formation of tetrahydronaphthalene, the one nucleus only being saturated. The further reduction to a completely saturated perhydronaphthalene takes place very slowly.

Naphthalene under similar conditions yields no tetrahydronaphthalene at any stage of the process, but a mixture of naphthalene and perhydronaphthalene, $C_{10}H_{18}$, is always obtained. This behaviour is not in accord with an aromatic-olefinic structure for naphthalene, such as proposed by Willstätter and Waser (A., 1912, i, 18). E. F. A.

Derivatives of *p*-Xylene. JAN J. BLANKSMA (*Chem. Weekblad*, 1913, 10, 136—141. Compare A., 1910, i, 661).—The melting-point curve of mixtures of 2 : 3-dinitro-*p*-xylene and 2 : 6-dinitro-*p*-xylene has been plotted, and a number of derivatives of *p*-xylene have been prepared. The curve indicates the formation of an additive product containing equimolecular proportions of the two substances.

Reduction of 2 : 5-dinitro-*p*-xylene with ammonium sulphide yields

5-nitro-*p*-2-xylidine, m. p. 142°, converted by Sandmeyer's reaction into 2-bromo-5-nitro-*p*-xylene, colourless crystals, m. p. 70°, which is reduced by iron powder and sulphuric acid to 5-bromo-*p*-2-xylidine, colourless crystals, m. p. 96°. Acetic anhydride converts this substance into 5-*bromo*-2-*aceto*-p-2-*xylidide*, colourless crystals, m. p. 180°, also formed by the action of a solution of bromine in glacial acetic acid on 2-aceto-*p*-2-xylidide. On saponification it yields 5-bromo-*p*-2-xylidine, already mentioned. On substituting bromine for the amino-group by Sandmeyer's reaction, there is formed 2 : 5-dibromo-*p*-xylene, m. p. 75°, also produced by bromination of *p*-xylene.

Bromine dissolved in glacial acetic acid transforms 5-nitro-*p*-2-xylidine into 3-*bromo*-5-*nitro*-p-2-*xylidine*, pale yellow crystals, m. p. 125°, converted by acetic anhydride and a trace of concentrated sulphuric acid into 3-bromo-5-nitro-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 208°. Replacement of the amino-group in 3-bromo-5-nitro-*p*-2-xylidine produces 2 : 3-*dibromo*-5-*nitro*-p-*xylene*, colourless crystals, m. p. 99°.

Bromine in glacial acetic acid reacts with *p*-2-xylidine, forming 3 : 5-dibromo-*p*-2-xylidine, m. p. 65°, converted by diazotisation and the action of boiling alcohol into 2 : 6-*dibromo*-p-*xylene*, colourless plates of mother-of-pearl lustre, m. p. 32°, also obtained in an impure liquid form by the bromination of *p*-xylene. Nitration in presence of sulphuric acid converts 2 : 6-dibromo-*p*-xylene into 2 : 6-*dibromo*-3 : 5-*dinitro*-p-*xylene*, colourless crystals, m. p. 190°.

3 : 5-Dibromo-*p*-2-xylidine is converted by acetic anhydride and concentrated sulphuric acid into 3 : 5-dibromo-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 192° (not 165°, as stated in *Rec. trav. chim.*, 1906, 25, 362). This substance is transformed by nitric and sulphuric acid into 3 : 5-*dibromo*-6-*nitro*-2-*aceto*-p-2-*xylidide*, colourless crystals, m. p. 256°, which is hydrolysed to 3 : 5-*dibromo*-6-*nitro*-p-2-*xylidine*, yellow crystals, m. p. 176°, also formed by bromination of 6-nitro-*p*-2-xylidine. By diazotisation and the action of boiling alcohol, this substance yields 3 : 5-*dibromo*-2-*nitro*-p-*xylene*, colourless crystals, m. p. 83°, which is converted by nitric and sulphuric acid into 3 : 5-dibromo-2 : 6-dinitro-*p*-xylene, already mentioned.

Replacement of the amino-group in 6-nitro-*p*-2-xylidine by bromine by the Sandmeyer reaction produces 2-*bromo*-6-*nitro*-p-*xylene*, pale yellow crystals, m. p. 38°.   A. J. W.

Kinetics of Ammonium Salts. EDGAR WEDEKIND and F, PASCHKE (*Zeitsch. physikal. Chem.*, 1913, 82, 314—324).—Polemical, an answer to von Halban (A., 1911, i, 852 ; compare also A, 1909, ii, 722 ; 1908, i, 723 ; 1911, i, 628). Several new preliminary experiments are given. It is shown that the addition of an inactive non-decomposable salt to a chloroform solution of an active iodide does not decrease the dissociation of the active iodide, but brings about a double decomposition, thus :

$$d\text{-NMePrPh}(C_7H_7)I + r\text{-NMePrPh}(C_7H_7)\cdot NO_3 \rightleftarrows$$
$$r\text{-NMePrPh}(C_7H_7)I + d\text{-NMePrPh}(C_7H_7)\cdot NO_3,$$
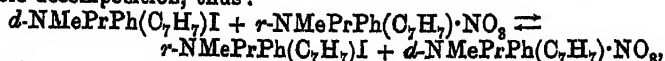
and of these four substances the iodides alone can dissociate, so that the decrease in the rate of dissociation, which is determined polari-

metrically, is explained.   The remaining and unchangeable activity is
due to the active nitrate which exists together with inactive nitrate in
the solution.   The latter can be precipitated by ether, and the amount
of active nitrate determined, which is always found to be equal in
concentration to that of the inactive nitrate added.   Preliminary
experiments are given on the rate of formation of phenylbenzylmethyl·
propylammonium bromide in chloroform solution at various tempera-
tures from methylpropylaniline and benzyl bromide.   J. F. S.

The Kinetics of Ammonium Salts.   Hans von Halban (*Zeitsch,
physikal. Chem.*, 1913, 82, 510—512).—Polemical, an answer to
Wedekind and Paschke's criticism (preceding abstract) of Halban's
paper (A., 1911, i, 852).   J. F. S.

Nitro-derivatives of Cresyl Oxides [Tolyl Ethers].   Alphonse
Mailhe (*Bull. Soc. chim.*, 1913, [iv], 13, 169—173).—Most of this
work has been published already (this vol., i, 173, 261). *p*-Tolyl ether
on nitration yields only a *tetranitro*-derivative, m. p. 84°, crystallising
in yellow needles, and furnishing on boiling with a dilute solution of
potassium hydroxide an amorphous, red powder which does not melt
at 300°.   T. A. H.

Nitro-derivatives of Cresylene Oxides [Tolylene Oxides].
Alphonse Mailhe (*Bull. Soc. chim.*, 1913, [iv], 13, 173—176. Com-
pare this vol., i, 261).—Part of this work has been published already
(*loc. cit.*). *p*-Tolylene oxide, m. p. 166°, on nitration in acetic acid
solution at 80° yields a mixture of the *mono*- and *dinitro*-derivatives.
The former has m. p. 197°, and is sparingly soluble in boiling alcohol.
The dinitro-derivative has m. p. 136°, and is readily soluble in boiling
alcohol ; it alone is formed when the nitration is effected in sulphuric
acid solution in the cold.   No higher nitro-derivative of the para-ether
could be obtained, whence the author considers that the union of the
two nuclei is in the ortho-position to the ether linking, whilst in
o-tolylene oxide (*loc. cit.*) it is in the meta-position.   T. A. H.

Preparation   of   Halogenated   Aminonaphtholsulphonic
Acids.   Farbenfabriken vorm Friedr. Bayer & Co. (D.R.-P.
254715).—Substituted aminonaphtholsulphonic acids can be readily
prepared by the halogenation of the *ON*-diacyl derivatives of 2-amino-
naphtholsulphonic acids with subsequent elimination of the acyl groups.
5-*Chloro*-6-*amino*-1-*naphthol*-3-*sulphonic acid* crystallises from water as
a colourless powder.   5-*Bromo-di*-p-*tolylsulphonyl*-6-*amino*-1-*naphthol*-
3-*sulphonic acid* is a yellow, crystalline powder.   The preparation
of 8-*bromo*-6-*amino*-1-*naphthol*-3-*sulphonic acid* is also described.
                                                          F. M. G. M.

3-Aminophenyl Mercaptan.   Theodor Zincke and Joh. Muller
(*Ber.*, 1913, 46, 775—786).—The preparation of 3-*aminophenyl
mercaptan* and of 3-*aminophenyl methyl sulphide* is described.   A
number of derivatives of the latter have been investigated.
Acetylaniline-m-*sulphonyl chloride*, $NHAc·C_6H_4·SO_2Cl$, is formed by

the action of phosphorus pentachloride on the corresponding sodium salt. It forms white needles, m. p. 88°, and is readily converted into the *amide*, m. p. 217°, and the *anilide*, m. p. 179°. Reduction of an alcoholic solution of the chloride by means of zinc dust transforms it into $3:3'$-*diacetylaminodiphenyl disulphide*, $S_2(C_6H_4\cdot NHAc)_2$, m. p. 210°, from which $3:3'$-*diaminodiphenyl disulphide*, colourless needles, m. p. 52°, is obtained by hydrolysis. The corresponding *hydrochloride* dissolves freely in water, whilst the *nitrate* and *sulphate* are sparingly soluble. When an alcoholic solution of the hydrochloride is boiled with sodium sulphide in the presence of a small quantity of sodium hydroxide, 3-aminophenyl mercaptan, b. p. 180—190°/16 mm., is formed as a pale yellow oil, which, when pure, is fairly stable towards air, but is readily oxidised when impure. Ferric chloride converts it into the disulphide. The *hydrochloride* and *sulphate* were examined. It forms a *diacetyl* derivative, m. p. 97°. With alcoholic benzaldehyde, it yields a *benzylidene* derivative, $CHPh(S\cdot C_6H_4\cdot N:CHPh)_2$, yellow powder, m. p. 59° (compare A., 1912, i, 257).

3-*Acetylaminophenyl methyl sulphide*, $NHAc\cdot C_6H_4\cdot SMe$, needles, m. p. 75°, is obtained by reducing $3:3'$-diacetylaminodiphenyl disulphide in alcoholic solution by means of sodium sulphide in the presence of sodium hydroxide and treatment of the product so obtained with methyl sulphate. Bromine converts it into a *perbromide*, which is readily transformed into a dibromo-substitution *product*. When a solution of it in chloroform is cooled in ice and saturated with chlorine, a pentachloro-*compound*, needles, m. p. 160°, probably having annexed formula, is obtained, which, when heated with aniline, yields triphenylguanidine and *dichloro-3-acetylaminophenyl mercaptan*, m. p. 152°. Hydrolysis of 3-acetylaminophenyl methyl sulphide by means of hydrochloric acid in aqueous alcoholic solution yields the *hydrochloride* of 3-aminophenyl methyl sulphide, from which the free *base*, pale yellow oil, b. p. 163—165°/16 mm., is obtained by means of ammonia. The *sulphate* was examined.
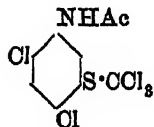
3-*Methylthiolphenyltrimethylammonium iodide*, $SMe\cdot C_6H_4\cdot NMe_3I$, m. p. 183—185° (decomp.), is obtained by the action of excess of methyl iodide on a methyl-alcoholic solution of 3-acetylaminophenyl methyl sulphide. It forms a di-iodo- and a tetra-iodo additive product. The free *base* is obtained by evaporation of its solution in a vacuum as yellowish-white, hygroscopic crystals.

3-*Methylthiolphenyltrimethylammonium chloride*, obtained from the corresponding iodide and silver chloride, forms white, hygroscopic needles. It yields a pale yellow, stable *platinichloride*, and an orange-yellow *dichromate*.

3-*Dimethylaminophenyl methyl sulphide*, pale yellow oil, b. p. 165—167°/16 mm., is obtained when the above iodide is heated above its m. p. under diminished pressure. It forms a readily soluble *hydrochloride* and *sulphate*.

3-Acetylaminophenyl methyl sulphide is oxidised by hydrogen peroxide in glacial acetic acid solution to the corresponding *sulphoxide*, $NHAc\cdot C_6H_4\cdot SO\cdot CH_3$, needles, m. p. 112°; this is converted by

hydrogen bromide into a *perbromide*, which readily passes into a mono-bromo-substitution *product*. When heated with aqueous alcoholic potassium hydroxide the above acetyl derivative is transformed into *3-aminophenylmethylsulphoxide*, colourless, rhombic leaflets, m. p. 115°. The *hydrochloride*, white needles, is readily soluble in water.

3-*Acetylaminophenylmethylsulphone*, $NHAc \cdot C_6H_4 \cdot SO_2Me$, obtained by the action of a larger quantity of hydrogen peroxide on a solution of 3-acetylaminophenyl methyl sulphide in glacial acetic acid (compare above), forms small, white needles, m. p. 137°, and is converted by aqueous alcoholic hydrogen chloride into 3-*aminophenylmethylsulphone*, m. p. 72°.

3-*Methylthiolbenzenediazonium chloride*, $SMe \cdot C_6H_4 \cdot N_2Cl$, is obtained in moderately stable, yellow leaflets by the addition of amyl nitrite to an alcoholic solution of the hydrochloride of 3-aminophenyl methyl sulphide in the presence of alcoholic hydrogen chloride. It couples with dimethylaniline and with β-naphthol, yielding dyes which crystallise in red needles. It decomposes when heated with water, but a phenol could not be isolated from the product of the reaction. It was transformed by the usual methods into 3-*methylthiolbenzonitrile*, white needles, m. p. 40° (3-*methylthiolbenzoic* acid, leaflets, has m. p. 129°), and 3-*methylthiolphenyl iodide*, almost colourless oil, b. p. 157°/16 mm.

3 : 3′-Diacetylaminodiphenyl disulphide is converted into the corresponding ammonium *iodide*, $S_2(C_6H_4 \cdot NMe_3I)_2$, m. p. 185—186° (decomp.), when heated with methyl alcohol and methyl iodide; this substance, when heated under diminished pressure, yields 3 : 3′-*dimethylaminodiphenyl disulphide*, $S_2(C_6H_4 \cdot NMe_2)_2$, colourless oil, b. p. 162—166°/16 mm. A solution of the latter in formic acid is converted by amyl nitrite in the presence of a little hydrochloric acid into 6 : 6′-*dinitroso*-3 : 3′-*dimethylaminodiphenyl disulphide*,

$$S_2(C_6H_3[NO] \cdot NMe_2)_2,$$

dark green needles, m. p. 130°, which is reduced by hydrogen sulphide in ammoniacal solution to 6-*amino*-2-*dimethylaminophenyl mercaptan*. The *hydrochloride* of the latter, white needles, m. p. 235° (decomp.), was investigated. It forms a colourless double *salt* with mercuric chloride. With potassium ferricyanide, it yields a dark green *precipitate*, the colour of which deepens on addition of alkali. Ferric chloride converts it into a dark red oxidation *product*, which yields a dark violet double *salt* with mercuric chloride. Hydrogen sulphide decomposes the latter, the original mercaptan being regenerated.

<div style="text-align:right">II. W.</div>

Basic Properties of Sulphoxides and their Position Among the Organo-metallic Bases. EMIL FROMM (*Annalen*, 1913, **396**, 75—103).—The similarities in behaviour between bases of the type $R_{n+1}Md \cdot OH$ (where Md represents a metalloid element such as N, P, As, Sb, O, S, Se, Te, or I, and n the number of atoms of hydrogen with which it can unite, and R an organic radicle) have frequently been emphasised. Compounds of the type MdR_n may be regarded as the anhydrides of $R_{n+1}Md \cdot OH$. All these bases are monoacidic.

The anhydrides, R_nMdO, of a second series of bases of the type $R_nMd(OH)_2$ are known. In the anhydrides, Md may be any one of the elements given above, but in the hydroxides hitherto Md has been only N, P, As, Sb, or Te. All these bases and their anhydrides are diacidic, and the anhydrides or their salts are characterised by the three equilibrium reactions: (i) $R_nMdO \rightleftharpoons R_nMd + O$; (ii) $R_nMdX_o \rightleftharpoons R_nMd + X_2$ (where X is halogen); (iii) $R_nMdCl_2 + H_2O \rightleftharpoons R_nMdCl \cdot OH + HCl \rightleftharpoons R_nMdO + 2HCl$.

In the present communication the author deals with substances in which Md is sulphur, and, therefore, $n = 2$. Sulphoxides can be prepared by reaction (i), the oxygen being supplied by nitric acid, hydrogen peroxide, or chromic acid, and also by reactions (ii) and (iii). The dichlorides of diaryl sulphides have been prepared by Fries and Vogt (A., 1911, i. 538), and are converted into sulphoxides by water; di-iodides of dialkyl sulphides, which have long been known, are, it is now shown, converted into sulphoxides by silver acetate.

It is also shown that sulphoxides can combine with one equivalent of hydrogen chloride to form hydrogen salts, $OH \cdot SR_2Cl$, and with two equivalents of hydrogen bromide or iodide to form normal salts, R_2SX_2, which are identical with the dibromides or di-iodides produced by reaction (ii). The hydrogen salts and the normal salts are both hydrolysed more or less rapidly by water, reproducing the sulphoxide. In addition to hydrolysis, the normal salts can also dissociate according to reaction (ii), and it depends on the relative velocities of dissociation and of hydrolysis whether a normal salt yields the sulphoxide or the sulphide by treatment with aqueous alkali hydroxide or silver acetate. The parent substance, H_2SO, of the sulphoxides, and its tautomeric form, $HS \cdot OH$, are unknown; anthraquinone derivatives of both have been described by Fries (A., 1912, i, 1005).

The relations between disulphides and disulphoxides and the basic properties of the latter can be represented by equations similar to (i), (ii), and (iii).

[With FRITZ SCHÄFER, AQUILA FORSTER, and BORIS VON SCHER-SCHEWITZKI.]—o-Nitrophenyl benzyl sulphide and the para-isomeride, 2 : 4-dinitrophenyl benzyl sulphide, dinitrophenyl methyl sulphide, and s-di-o-nitrophenylthiolethane, resemble di-p-tolyl sulphide (Fromm and Raiziss, A., 1910, i, 554) in not forming additive compounds with bromine; 2 : 4-dinitrophenyl benzyl sulphide in cold chloroform yields *bromodinitrophenyl benzyl sulphide*, $C_6H_3Br(NO_2)_2 \cdot S \cdot CH_2Ph$, m. p. 104°, yellow needles. Also the dibromides cannot be obtained from the sulphoxides and hydrogen bromide. Both reactions proceed, however, when the nitro-groups are reduced to amino-groups and the latter acetylated; thus di-o-acetylaminophenylthiolethane and bromine in cold chloroform yield the *tetrabromide*, $C_2H_4(SBr_2 \cdot C_6H_4 \cdot NHAc)_2$, m. p. 60—61°, unstable, orange crystals, which is converted by water into *di-*o-*acetylaminophenylsulphoxyethane*, $C_2H_4(SO \cdot C_6H_4 \cdot NHAc)_2$, m. p. 214°, colourless needles; the latter and hydrogen bromide in chloroform regenerate the tetrabromide.

Dibenzyl sulphide and chlorine in petroleum at 0° yield the very unstable *dichloride*, $SCl_2(CH_2Ph)_2$, which is converted into the sulphoxide by water. The dibromide is more stable (Fromm and

Raiziss, *loc. cit.*). The *di-iodide*, $SI_2(CH_2Ph)_2$, m. p. 64—65°, violet crystals, prepared from the sulphide and iodine in glacial acetic acid on the water-bath, is extremely stable. It is decomposed, without hydrolysis, by dilute sodium hydroxide, dibenzyl sulphide being regenerated; the hydrolysis is effected by silver acetate in dilute acetic acid, whereby dibenzylsulphoxide is produced.

Dibenzylsulphoxide and hydrogen iodide in chloroform at 0° yield the preceding dibenzyl sulphide di-iodide. The sulphoxide and hydrogen chloride in benzene form *dibenzylsulphoxide hydrochloride*,

$$OH \cdot SCl(CH_2Ph)_2,$$
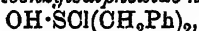
m. p. 90°, colourless crystals, which does not further react with hydrogen chloride, and is decomposed into the sulphoxide by water or in a vacuum.

s-Dibenzylthiolethane reacts with chlorine in cold petroleum to form the unstable *tetrachloride*, $C_2H_4(SCl_2 \cdot CH_2Ph)_2$, white crystals, with bromine in cold chloroform to form the moderately stable *tetrabromide*, m. p. 84°, orange-red crystals, and with iodine in boiling glacial acetic acid to form the *tetraiodide*, m. p. 94°, red needles. The tetrachloride and the tetrabromide are very rapidly converted into the disulphoxide by water. On the contrary, the disulphoxide suspended in cold petroleum or chloroform is converted into the tetrabromide by hydrogen bromide, and into a comparatively stable *dihydrochloride*,

$$C_2H_4[SCl(OH) \cdot CH_2Ph]_2,$$
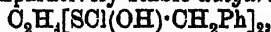
by hydrogen chloride.

p-*Tolyl benzyl sulphide*, $C_6H_4Me \cdot S \cdot CH_2Ph$, m. p. 44°, prepared from *p*-tolyl mercaptan and benzyl chloride, yields the *sulphoxide*, m. p. 136—137°, by oxidation with 30% hydrogen peroxide in glacial acetic acid or with nitric acid, and reacts with chlorine or bromine in cold petroleum to form respectively the very unstable *dichloride*, $C_6H_4Me \cdot SCl_2 \cdot CH_2Ph$, and comparatively unstable *dibromide*, and with iodine in hot glacial acetic acid to form the stable *di-iodide*, m. p. 72°, dark blue plates. The dichloride and the dibromide by treatment with water, and the di-iodide by treatment with silver acetate, are converted into *p*-tolylbenzylsulphoxide; the di-iodide and aqueous sodium hydroxide yield *p*-tolyl benzyl sulphide. The dibromide and the di-iodide are obtained from the sulphoxide and hydrogen bromide or iodide in chloroform. p-*Tolyl methyl sulphide di-iodide*, $C_6H_4Me \cdot SMeI_2$, m. p. 40°, prepared from its components in petroleum, crystallises in dark blue needles.

Formaldehyde-*p*-tolylmercaptal (this vol., i, 176) forms a *tetraiodide*, $CH_2(SI_2 \cdot C_6H_4Me)_2$, m. p. 68—70°, which can also be obtained from the disulphoxide and hydrogen iodide in chloroform, and is not converted into the disulphoxide by silver acetate. Formaldehydebenzyl-mercaptal also forms a *tetraiodide*, $CH_2(SI_2 \cdot CH_2Ph)_2$, decomp. 110—140°, which is converted by silver acetate, not into the sulphoxide as usual, but into formaldehydebenzylmercaptal.

In boiling glacial acetic acid, benzyl disulphide and iodine form the *tetraiodide*, $S_2(CH_2Ph)_2I_4$, decomp. 113—120°, green crystals, which is converted into the disulphoxide by silver acetate in hot glacial acetic acid; from the latter the tetraiodide is regenerated by hydrogen iodide at −5° in carbon tetrachloride. *Benzyl disulphide tetrachloride* is

extremely unstable, and the *tetrabromide* has m. p. 2° (decomp.); the latter and silver acetate yield the disulphoxide.   C. S.

Substituted Aryl Sulphonamides. OTTO N. WITT and D. UERMÉNYI (*Ber.*, 1913, 46, 296—308).—Hinsberg's method for the preparation of secondary bases (A., 1891, 49) has not yet received general application, owing to the difficulty which has been experienced in hydrolysing the sulphonamides. For this purpose Schroeter and Eisleb (A., 1909, i, 575) dissolved the substances in cold concentrated sulphuric acid, but obtained in the case of benzenesulphonanilide, not aniline but sulphanilic acid. It is now shown that good results may be obtained with 80% sulphuric acid. The toluene-*p*-sulphonamide is suspended in this acid and heated to 135—150°, when solution and hydrolysis take place. On cooling, *p*-toluenesulphonic acid separates, and is removed by filtration, whilst the base is liberated from the diluted filtrate and distilled in steam. The yields are somewhat impoverished by the formation of non-volatile by-products, which occur to a preponderating extent in the case of ethyl-*p*-toluidine, and consist of a sulphone, being due to the displacement of the *p*-toluenesulphonic acid residue into the ring.

Toluene-*p*-sulphon-*p*-toluidide and also its *acetyl* derivative, m. p. 133·5°, give *p*-toluidine-*m*-sulphonic acid with concentrated sulphuric acid, but sulphonation of the base does not occur with 80% acid at 150°. Crude methyl- and ethyl-aniline and also methyl-*o*-toluidine (*toluene-*p*-sulphon-methyl-o-toluidide*, $C_{15}H_{17}O_2NS$, has m. p. 119—120°) may be conveniently purified by this process. *Toluene-*p*-sulphonethyl-o-toluidide*, $C_{16}H_{19}O_2NS$, forms long needles, m. p. 75°, but the ethyl-*o*-toluidine is accompanied by a small quantity of the rearranged *sulphone*, white needles, m. p. 134°. The hydrolysis of *toluene-*p*-sulphonethyl-*p*-toluidide*, colourless needles, m. p. 71—72°, gives less than a 50% yield of ethyl-*p*-toluidine, the chief product being precipitated on adding water, in colourless needles, m. p. 113°. It is formed in still greater quantity when concentrated acid is used, and is a secondary base, since it gives an *acetyl* compound, $C_{16}H_{18}O_2NS \cdot O_2H_3O$, in silky, white needles, m. p. 143—144°. When the base is heated at 275° in a current of hydrogen chloride, ethyl chloride is removed and the resulting primary *aminoditolylsulphone*, $C_{14}H_{15}O_2NS$, colourless crystals, m. p. 169°, may be diazotised and deprived of the amino-group. The resulting compound forms colourless needles, m. p. 116°, and can be synthesised by condensing the chloride of *m*-toluenesulphonic acid with toluene by means of aluminium chloride. It is, therefore, mp-*ditolylsulphone*, and the rearrangement of the sulphonamide into a sulphone is to be represented thus:

(p) Me·C_6H_4·SO_2 (p) Me·C_6H_4·SO_2
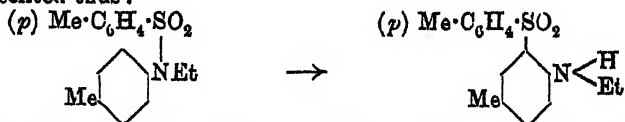
The sulphone may be nitrated in the cold, and the *mononitro*-derivative, intensely yellow needles, m. p. 161°, forms an *acetyl* compound, $NO_2 \cdot C_{16}H_{17}O_2NS \cdot C_2H_3O$, in colourless crystals, m. p. 159—160°.   J. C. W.

Preparation of p-Alkyloxyphenylaminoalkyl Sulphites. FARB-WERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 255305).—When acetaldehyde (or its higher homologues) is condensed with p alkyloxy-aminobenzenes in the presence of an alkali (or ammonium) hydrogen sulphite it furnishes salts of therapeutic value, and having the general formula OR$^1\diagdown\diagup$NH·CHR·O·SO$_2$M, where M is an alkali metal or ammonium, R = methyl or ethyl, and R^1 an alkyl group.

Sodium p-*phenetidinoethyl sulphite*, needles, is obtained when a cooled aqueous solution of 40% sodium hydrogen sulphite (110 parts) is treated with acetaldehyde (20 parts) and p-phenetidine (55 parts), and subsequently gently heated until a clear solution is obtained; on cooling, the solution sets to a crystalline mass.

The p-phenetidine can be replaced by p-anisidine, and the acetalde-hyde by propaldehyde. F. M. G. M.

Preparation of Aromatic Amino-alcohols FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 254438).—The reduction of aromatic ketones to the corresponding alcohols has previously been described, and is now found to proceed quantitatively if hydrogen is employed in the presence of colloidal metals of the platinum group.

OMe$\diagdown\diagup$CH(OH)·CHMe·NH$_2$
OMe
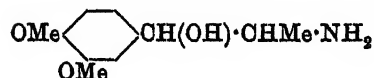
3 : 4-*Dimethoxyphenyl-a-propanol-amine* (annexed formula), hard, colourless crystals, m. p. 138°, is obtained when 100 parts of α-aminopropionylveratrole (A., 1910, i, 313) in 300 parts of water with palladous chloride (5 parts), gum arabic (10 parts), and hydrazine hydrate are submitted to the action of hydrogen during two days at 20° and under a pressure of 1·5 atmo-

OH$\diagdown\diagup$CH(OH)·CHMe·NH$_2$
OH

spheres; the *hydrochloride*, colour-less leaflets, has m. p. 212°; whilst the reduction in a similar manner of 4-*a-aminopropionylcatechol* (A., 1910, i, 313) gives rise to a 95% yield of 3 : 4-*dihydroxyphenyl-a-propanolamine* (annexed formula), m. p. 188°; the *hydrochloride*, a colourless powder, has m. p. 95°. F. M. G. M.
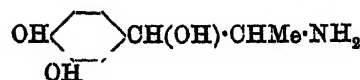
Preparation of Esters of Nitroanthraquinonylanthranilic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 254475).—When nitroaminoanthraquinones are treated with the esters of o-halogenated benzoic acids in the presence of copper (or a salt of copper), they give rise to nitroanthraquinonylanthranilic acid esters.

Methyl 4-nitro-1-anthraquinonylanthranilate, reddish-brown needles, m. p. 234—240°, is thus obtained from 1-nitro-4-aminoanthraquinone and methyl o-chlorobenzoate. On hydrolysis and subsequent reduction, these compounds furnish the corresponding aminoanthraquinonyl-anthranilic acids, which are of technical value. F. M G. M.

Metaquinonoids. OTTO STARK and O. GARBEN (*Ber.*, 1913, **46**, 659—666).—The method by which Thiele and Balhorn obtained yellow

tetraphenyl-p-xylylene from methyl terephthalate (A , 1901, i, 491) has been applied to methyl isophthalate, and a yellow tetraphenyl-m-xylylene of the annexed formula has been prepared.
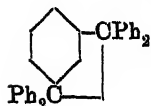
*Tetraphenyl-*m-*xylylene glycol*, $C_{32}H_{26}O_2$, is obtained by the action of magnesium phenyl bromide on methyl isophthalate in a boiling mixture of benzene and anisole. It crystallises from glacial acetic acid with one molecule of the solvent in light yellow prisms, m. p. 88°, and from light petroleum in the free state, m. p. 112—113°. Hydrogen chloride precipitates from an acetic acid solution the *dichloride*, $C_{32}H_{24}Cl_2$, which crystallises from petroleum in white needles, m. p. 137°, and like the *dibromide*, m. p. 167—168°, can be titrated with alkali in alcoholic solution. When heated with zinc dust and Devarda's alloy in benzene (compare Schmidlin, A., 1908, i, 150), a golden-yellow solution with red fluorescence is obtained, from which petroleum precipitates *tetraphenyl*-m-*xylylene*, in yellow needles, m. p. 210—220° (decomp.). It gives the above dichloride with chlorine, but is stable towards oxygen.

When hydrogen chloride is passed into the acetic acid mother liquors of the glycol, a *dichloride* is obtained, which is insoluble in hot petroleum, and has m. p. 236—238°. It may be hydrolysed and converted into a *dimethyl ether*, $C_{34}H_{30}O_2$, m. p. 187—188°, from which the *dibromide*, m. p. 242°, is obtained. It is supposed that the $-C(OH)Ph_2$ group has wandered into the *para*-position and that the compounds are isomeric, according to Schmidlin's isomerism (A., 1912, i, 32), with tetraphenyl-p-xylylene glycol dimethyl ether, m. p. 181—182·5°, and tetraphenyl-p-xylylene dibromide, m. p. 270—272° (Thiele and Balhorn, *loc. cit.*).   J. C. W.

Direct Hydrogenation of the Phenylacetic Esters. Preparation of *cyclo*Hexylacetic Acid. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, 156, 424—427. Compare A., 1912, i, 353).—The esters of phenylacetic acid are readily hydrogenated by excess of hydrogen in the presence of very active nickel at 180°. By this means the following esters have been prepared.

Methyl cyclo*hexylacetate*, b. p. 200—202° (corr.), D_0^0 0·9961, D_0^{14} 0·9896, n_D^{14} 1·459. Ethyl *cyclo*hexylacetate, b. p. 211—212° (corr.), D_0^0 0·9626, D_0^{14} 0·9537, n_D^{14} 1·451 (compare Freundler, A., 1905, i, 890). *Propyl* cyclo*hexylacetate*, b. p. 228—229° (corr.), D_0^0 0·9560, D_0^{15} 0·9431, n_D^{15} 1·450. iso*Butyl* cyclo*hexylacetate*, b. p. 240—241° (corr.), D_0^0 0·9445, D_0^{14} 0·9307, n_D^{14} 1·452. iso*Amyl* cyclo*hexylacetate*, b. p. 250—251° (corr.), D_0^0 0·9388, D_0^{16} 0·9267, n_D^{16} 1·454.

The refractive indices are practically constant throughout, but the density diminishes regularly with increase in molecular weight. All these esters are readily saponified by alcoholic potassium hydroxide, giving the free acid, m. p. 32°.

The phenylpropionic esters undergo similar hydrogenation.

It is of interest to note that benzyl acetate, the isomeride of methyl phenylacetate, submitted to similar hydrogenation is decomposed, giving

toluene and acetic acid, at the same time destroying the activity of the nickel.

<div align="right">W. G.</div>

Esters of Cellulose with Benzoic Acid and its Derivatives. OTTO HAUSER and H. MUSCHNER (*Zeitsch. angew. Chem.*, 1913, **26**, 137—139).—In the preparation of the esters the authors used hydrocellulose, which was made according to the method of Girard. The hydrocellulose is treated, under cooling, with a large excess of benzoyl chloride and sodium hydroxide, and the resulting product washed with hot water to remove alkali, and finally with alcohol and ether. The results show that the product obtained is always cellulose monobenzoate; no dibenzoate is formed, whatever may be the concentration of the sodium hydroxide (compare Cross and Bevan, A., 1901, i, 452). The only effect of the concentration of the sodium hydroxide is on the time of reaction, the stronger the alkali the shorter the time. The best concentration is 20%, and the temperature should be kept at 20° by appropriate cooling.

*Cellulose mono-*p-*chlorobenzoate,* $C_{19}H_{28}O_{11}Cl$, was prepared similarly from hydrocellulose and *p* chlorobenzoyl chloride. It is an amorphous, white powder, insoluble in all solvents, non-hygroscopic and non-fusible. Esters could not be obtained from *m*-nitrobenzoyl chloride and *p*-bromobenzoyl chloride, owing to the fact that the high temperature necessary to melt the chloride resulted in its saponification by the sodium hydroxide before the cellulose entered into reaction. *p*-Toluoyl chloride gave a product corresponding with the formula $C_{18}H_{26}O_{11}$, instead of the expected formula $C_{20}H_{26}O_{11}$.

<div align="right">T. S. P.</div>

An Interesting Case of Dimorphism. ALEXIS DUFFOUR (*Compt. rend.*, 1913, **156**, 473—475).—Vanillyl benzoate is obtained in two distinct crystalline forms, monoclinic or triclinic, accordingly as it is prepared by the hydrogenation of vanillin benzoate in the cold in the presence of platinum black (compare Vavon, A., 1912, i, 260), or by the condensation of benzoyl chloride and sodium vanillyloxide. These two forms are both stable at the ordinary temperature, having been kept for a year unaltered. The triclinic crystals

$$[a:b:c=0.8697:1:0.5283;\ a=90°20';\ \beta=72°22';\ \gamma=72°44']$$

have m. p. 99°, whilst the monoclinic

$$[a:b:c=0.7814:1:1.3460;\ \beta=111°9'],$$

observed under a microscope, begin to melt at 90°, and in the liquid obtained, triclinic crystals begin to form, transforming the whole into a friable mass only melting at 99°. This transformation of the monoclinic into the triclinic form when the two are in contact is retarded by diminution in temperature and becomes inappreciable at 30°.

<div align="right">W. G.</div>

Nitration of Benzoic Acid in the Presence of Mercury RICHARD WOLFFENSTEIN and W. PAAR (*Ber.*, 1913, **46**, 589—599).— When benzoic acid (50 grams) is nitrated with nitric acid (300 grams; D = 1·35) in the presence of mercuric nitrate, 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid is obtained. The mixture is heated on the brine-bath at

105° for twenty hours, after which it is filtered from unchanged benzoic acid, the filtrate made alkaline to remove the mercury, acidified, and then extracted with ether to dissolve out any m-nitrobenzoic acid formed. The aqueous solution is then concentrated in order to obtain crystals of the readily soluble 2 : 4 : 6-trinitro-m-hydroxybenzoic acid. Various trinitrohydroxybenzoic acids have been described in the literature, and in order to compare them with the above acid they have been again prepared by the authors. Shardinger (A., 1876, 584) obtained an acid by the nitration of anthraflavone. Since anthraflavone is a mixture of the two isomerides, anthraflavic acid and 1 : 7-dihydroxyanthraquinone, the authors have nitrated each of these substances. In each case a tetranitro-derivative is first obtained, which undergoes fission, on further action of nitric acid, with the formation of the above-mentioned 2 : 4 : 6-trinitro-m-hydroxybenzoic acid. The third isomeride of anthraflavic acid is anthrarufin, the tetranitro-derivative of which has been prepared by Liebermann (A., 1879, 537). This on boiling with nitric acid undergoes fission with the formation of the above acid. Tetranitroanthrarufin is therefore 3 : 4 : 6 : 8-tetranitro-1 : 5-dihydroxyanthraquinone. Beilstein and Geitner (*Annalen*, 1866, 139, 12) obtained a trinitrohydroxy-acid by the action of fuming nitric acid on m-aminobenzoic acid, and this the authors prove to be identical with their acid.

2 : 4 : 6-Trinitro-m-hydroxybenzoic acid, $C_7H_3O_9N_3$, crystallises with one molecule of water of crystallisation, in rhombic tablets ; m. p. 180°. It forms a series of salts, characterised by their water of crystallisation. The *sodium, potassium, barium,* and *silver* salts have $2H_2O$, and the *copper* salt, $5H_2O$. Its constitution was proved by its conversion into picric acid when heated in small quantities (0 2 gram) at a time at 195°. The simplest method of preparation is from m-hydroxybenzoic acid. Five grams of this acid are dissolved in 30 grams of fuming nitric acid (D = 1·52), and the solution heated on the water-bath. The nitric acid is expelled on the water-bath, the residue again evaporated down with nitric acid, then with water, and finally extracted with benzene, leaving the pure acid.   T. S. P.

2 : 4 : 6-Trinitro-m-hydroxybenzoic Acid. RICHARD WOLFFEN-STEIN and W. PAAR (*Ber.*, 1913, 46, 680—682. Compare preceding abstract).—E. F. Smith (*Proc. Amer. Phil. Soc.*, 25) described a compound, which he obtained by treating ethyl m-hydroxybenzoate with nitrous acid and then with an excess of potassium hydroxide, as a trinitro-m-hydroxybenzoic acid, basing his formula on an estimation of potassium in the monopotassium salt. It might be expected that the hydroxyl hydrogen should also have been replaced by potassium and that the acid might be identical with Wolffenstein and Paar's compound. These authors have repeated Smith's experiment, and find that the product is in reality an ester which cannot be hydrolysed by prolonged boiling with alcoholic or aqueous potash, and is therefore, according to Victor Meyer's rule that ortho-substituents protect a carboxyl or ester group, *ethyl* 2 : 6-*dinitro*-m-*hydroxybenzoate*. It has m. p. 117°.
                                                                J. C. W.

Action of Hydrogen Cyanide on *p*-Nitrobenzaldehyde.
GUSTAV HELLER [with OTTO FRITSCH] (*Ber.*, 1913, **46**, 280—294)
—When *p*-nitrobenzaldehyde is suspended in glacial acetic acid and
shaken with a concentrated aqueous solution of potassium cyanide
until dissolved, it is converted into *p*-nitromandelonitrile, which may
be precipitated by water. The behaviour of this substance towards
various reagents, its conversion into nitro- and amino-mandelic acid,
and attempts to form anhydrides of the latter acid are described.

p-*Nitromandelonitrile*, $NO_2 \cdot C_6H_4 \cdot CH(OH) \cdot CN$, crystallises from
benzene in faintly yellow needles, m. p. 109—110°, which on hydrolysis
with hydrochloric acid readily yield *p*-nitromandelic acid. Towards
sodium hydroxide it is very sensitive, and from the product of the re-
action, *p*-nitroso-, *p*-nitro-, and *p* azoxy-benzoic acids have been isolated.

a-*Benzoyloxy*-p-*nitrophenylacetic* acid, $NO_2 \cdot C_6H_4 \cdot CH(OBz) \cdot CO_2H$, is
obtained by benzoylating the acid in pyridine solution, in yellowish-
white prisms, m. p. 185—186°. It is easily hydrolysed, and all
attempts to reduce it resulted in the production of benzoic acid. The
reduction of *p*-nitromandelic acid itself follows different courses ; with
zinc and acetic acid it results in p-*azoxymandelic acid*, $C_{18}H_{14}O_7N_2$,
in yellow needles, which darken at 190°; with stannous chloride the
product is *p*-aminophenylacetic acid; ferrous sulphate and ammonia
lead to p-*aminomandelic* acid, $NH_2 \cdot C_6H_4 \cdot CH(OH) \cdot CO_2H$, which forms
faintly yellow needles from warm water, and a colourless *hydrochloride*.
When warmed for a long time in water, it gradually deposits a yellow
anhydride, $(C_8H_7O_2H)_x$, m. p. 210° (decomp.), which is insoluble in
organic solvents. *p*-Aminomandelic acid yields a normal *benzoyl*
derivative in sodium carbonate solution as a crystalline powder, m. p.
218°, which does not lose water when heated with acetic anhydride, but

when benzoylated in pyridine in the cold, the
product is β-*hydroxy*-1-*benzoylindole* (annexed
formula).
This substance could only be obtained as a
colourless, amorphous powder, which was not
readily attacked by warm aqueous alkali, but
was hydrolysed by cold alcoholic potash to *p*-benzoylamino-
mandelic acid.
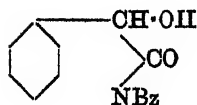
If the solution of *p*-nitrobenzaldehyde in concentrated potassium
cyanide and acetic acid is not immediately precipitated by water,
but is left for a day, pp'-*dinitrodeoxybenzoin cyanide*,
$$NO_2 \cdot C_6H_4 \cdot CO \cdot CH(CN) \cdot C_6H_4 \cdot NO_2,$$
is deposited. This crystallises in pale yellow needles, m. p.
267—268°, cannot be acetylated, and gives no reaction with ferric
chloride. On reduction it yields *p*-aminobenzoic acid, and when
dissolved in hot sodium hydroxide it deposits *p*-azoxybenzoic acid.
When the red solution in cold sodium hydroxide is at once filtered into
hydrochloric acid, however, 4-*nitro*-4'-*nitrosostilbene*-αβ-*diol*,
$$NO_2 \cdot C_6H_4 \cdot C(OH) \cdot C(OH) \cdot C_6H_4 \cdot NO,$$
can be extracted by means of boiling water from the precipitate. It
forms colourless leaflets, m. p. 225° (decomp.), which give an intense,
dark red colour with ferric chloride, and form acetyl and benzoyl
derivatives which could not be obtained pure. J. C. W.
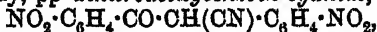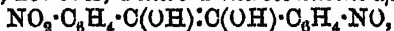
Preparation of Carboxydiarylhydrols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254122).—6-*Hydroxy*-2 : 4 *dimethylbenzoic acid*, m. p. 66°, is prepared by the action of carbon dioxide on *s*-xylenol; when it is slowly added to a cooled solution of *p*-diethylaminobenzaldehyde (1 mol.) in concentrated sulphuric acid, it gives rise to a *hydrol*, which can be further condensed with *o*-hydroxytoluic acid to yield *compounds*, which dye wool in violet shades.

Similar *compounds* are also described from *o*-chloro-*p*-diethylaminobenzaldehyde with *m*-hydroxytoluic acid, and its further condensation with *o*-hydroxytoluic acid; from *o*-chlorobenzaldehyde with 6-hydroxy-2:4-dimethylbenzoic acid, followed by condensation with *o*-hydroxytoluic acid, whilst the tinctorial properties of other similar compounds are tabulated in the original.   F. M. G. M.

Preparation of 2-Halogen-5-acylaminobenzoylbenzoic Acid. AKTIEN-GESELLSCHAFT FUR ANILIN-FABRIKATION (D.R.-P. 254091).— 3-Aminobenzoylbenzoic acid (annexed formula) and its homologues can be readily acetylated by ordinary methods, and on subsequent halogenation (in the same solution) yield 2-halogen-5-acetylaminobenzoylbenzoic acid.
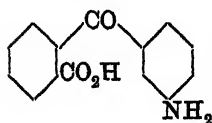
The following compounds are described: 6-*Bromo*-3-*acetylaminobenzoylbenzoic acid*, hard crystals, m. p. 218°; 6-*bromo*-3-*acetylamino*-p-*toluoylbenzoic acid* (prepared from 3-amino-*p*-toluoylbenzoic acid), colourless needles, m. p. 226°; 2-*bromo*-5-*acetylamino*-4-*carboxybenzoylbenzoic acid* (from 3-amino-4-carboxybenzoylbenzoic acid, m. p. 265°), short, colourless, rod-like crystals, m. p. 264—266°, and 2-*chloro*-5-p-*toluenesulphonyl*-p-*toluoylbenzoic acid*, colourless rods, m. p. 135°.   F. M. G. M.

α-Hydroxy-γ-phenylcrotonic Acid. An Example of an Ether of a Ketone Hydrate. J. BOUGAULT (*Compt. rend.*, 1913, 156, 555—556).—The acid amide, $C_{20}H_{23}O_6N$, obtained by the hydrolysis of α-hydroxy-γ-phenylcrotonamide (compare this vol., i, 269) on treatment with potassium permanganate in dilute acid solution gives a *compound*, $C_{20}H_{19}O_8N$, m. p. 120°, to which the author assigns the annexed constitution. The presence of the imide group in the compound is shown (1) by its pseudo-acid properties; (2) by its transformation into an *acid amide*, $C_{20}H_{21}O_4N$, m. p. 171°, and finally to the dibasic *acid*, $C_{20}H_{20}O_5$, m. p. 204°, by the action of dilute alkali hydroxides; (3) by the formation of a N-*methyl* derivative, m. p. 86°, which liberates methylamine on treatment with alkali. The compound, unlike the acid amide from which it is prepared (*loc. cit.*), is not readily decomposed by alkalis to give benzylpyruvic acid. Its preparation by the elimination of two tertiary hydroxyl groups appears to be the reverse of Wagner's action.   W. G.
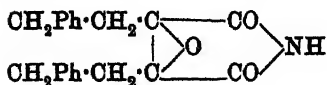
Preparation of Esters of Acetylsalicylic [o-Acetoxybenzoic] Acid. RICHARD WOLFFENSTEIN and JOSEF ZELTNER (*Ber.*, 1913, 46, 582—586).—Attempts to prepare ethyl o-acetoxybenzoate by the action of o-acetoxybenzoyl chloride on ethyl alcohol led to the isolation of ethyl salicylate, ethyl acetate, salicylic acid, and salicylic anhydride, the primarily formed ethyl o-acetoxybenzoate being decomposed by the hydrogen chloride liberated during the reactions. Satisfactory results were, however, obtained when the reaction was carried out in the presence of a substance capable of absorbing hydrogen chloride, for example, quinoline.

*Trichloro*isopropyl o-*acetoxybenzoate* was obtained by heating a a mixture of o-acetoxybenzoyl chloride, trichloroisopropyl alcohol, and dimethylaniline on the water-bath during two hours. It had m. p. about 65°, and could not be distilled without decomposition. Occasionally this ester was obtained in an oily form, which could not be caused to crystallise, but which, according to analysis, was pure.

Trichloro-tert.-*butyl* o-*acetoxybenzoate*, m. p. 55—57°, after previous softening, b. p. about 180°/16 mm. (slight decomp.), was obtained by heating o-acetoxybenzoyl chloride and *tert.*-trichlorobutyl alcohol at 140° in the presence of barium carbonate. H. W.

Preparation of Chloroanthraquinonecarboxylic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 255121).—The method previously described (A., 1911, i, 466), in which anthraquinone was chlorinated in sulphuric acid solution in the presence of iodine, has now been extended to the anthraquinone-α- and β-carboxylic acids.

When anthraquinone-β-carboxylic acid dissolved in fuming sulphuric acid (in the presence of iodine) is chlorinated at 125°, it gives rise to a *dichloroanthraquinonecarboxylic acid*, yellow crystals, m. p. above 300°, which when heated with p-toluidine furnishes an intensely green quinazarin-like derivative, thus indicating that the chlorine atoms are in the para-position with regard to each other.

The analogous compound from anthraquinone-α-carboxylic acid crystallises from acetic acid, and has m. p. 240—241°. The anthraquinonedicarboxylic acids can also be employed in this reaction. F. M. G. M.

Saturated δ-Ketonic Esters and their Derivatives. DOROTHY A. HAHN AND ANGIE G. ALLBEE (*Amer. Chem. J.*, 1913, 49, 171—179).— Kohler (A., 1911, i, 384) has described a general method for the preparation of unsaturated δ-ketonic esters; this method has now been applied to the production of the corresponding saturated compounds.
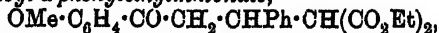
Ethyl β-anisoyl-α-phenylethylmalonate,
$$OMe \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CHPh \cdot CH(CO_2Et)_2,$$
m. p. 78°, obtained by the condensation of ethyl malonate with anisyl styryl ketone in presence of piperidine, crystallises in plates or stout needles. The corresponding *methyl* ester, m. p. 104°, forms plates or slender needles. When an alcoholic solution of the ethyl ester is treated with concentrated aqueous solution of potassium hydroxide, the *potassium* salt of β-anisoyl-α-phenylethylmalonic acid separates, which

is converted by acids into the *potassium hydrogen* salt and subsequently into the acid itself.   *β-Anisoyl-α-phenylethylmalonic acid*, m. p. 165° (decomp.), crystallises from water in slender needles containing water of crystallisation, which is eliminated below 130°.   By the action of bromine on a solution of ethyl β-anisoyl-α-phenylethylmalonate in chloroform, the *β-bromo*-derivative,

$$OMe \cdot C_6H_4 \cdot CO \cdot CHBr \cdot CHPh \cdot CH(CO_2Et)_2,$$
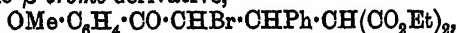
m. p. 97°, is obtained, which forms large, six-sided prisms.

When β-anisoyl-α-phenylethylmalonic acid is heated at 165—170° until the evolution of carbon dioxide ceases, *γ-anisoyl-β-phenylbutyric acid*, $OMe \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CHPh \cdot CH_2 \cdot CO_2H$, m. p. 152°, is obtained, which crystallises in plates or prisms; its *methyl* ester, m. p. 86°, forms long plates or prisms, and is hydrolysed by potassium hydroxide with formation of the *potassium* salt, which crystallises with $1H_2O$.   On the addition of bromine to a solution of γ-anisoyl-β-phenylbutyric acid in chloroform, two isomeric γ-*bromo*-derivatives,

$$OMe \cdot C_6H_4 \cdot CO \cdot CHBr \cdot CHPh \cdot CH_2 \cdot CO_2H,$$
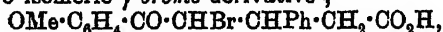
are obtained with m. p. 144° (decomp.) and 119° respectively, which both behave in the same way when treated with sodium carbonate, yielding *γ-anisoyl-β-phenyl-γ-butyrolactone*,

$$OMe \cdot C_6H_4 \cdot CO \cdot CH {<}^{CHPh}_{O-CO}{>} CH_2,$$
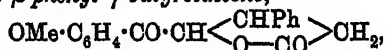
m. p. 109°, which forms large, six-sided prisms.   The methyl ester also yields two γ-*bromo*-derivatives, m. p. 84° and 122°.   E. G.

A New Oxide of Carbon, $C_{12}O_9$. HANS MEYER and KARL STEINER (*Ber.*, 1913, **46**, 813—815).—When mellitic acid is subjected to the action of dehydrating agents, either it remains unchanged or, by more drastic treatment, it is converted into the anhydride of pyromellitic acid.   As intermediate product, an anhydrocarboxylic *acid* (annexed formula) appears to be formed.   This substance can be isolated in the pure state by prolonged boiling of mellitic acid with thionyl chloride or by heating these substances at 160° during several hours.   It forms a white, crystalline powder, which unites with the calculated quantity of water to form mellitic acid, and which, when strongly heated, yields pyromellitic anhydride and carbonised products.
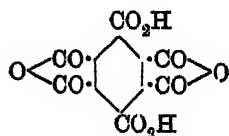
The *oxide* [*mellitic anhydride*] (annexed formula) is obtained when mellitic acid is boiled under reflux with much benzoyl chloride during six hours.   It separates from boiling benzoyl chloride in colourless crystals, which are perfectly stable and non-hygroscopic.   It is practically insoluble in cold water, but unites with warm water to form mellitic acid.   It gives characteristic colorations with various solvents of high b. p.; thus with naphthalene, retene, phenanthrene, and fluorene it yields rose-red to bluish-red solutions, and with nitrobenzene a bluish green solution.   It darkens when heated above 320°.   H. W.
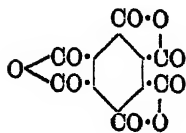
Constituents of Essential Oils. [Degradation of the Diketone, $C_{13}H_{20}O_2$, Obtained from Selinene.] FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1913, 46, 599—603. Compare this vol., i, 66, 188).—The diketone, $C_{13}H_{20}O_2$, obtained by the oxidation of natural selinene and also the diketo-monocarboxylic acid, obtained by the action of ozone on ortho(α)selinene, have been further oxidised, whereby a tribasic acid, $\begin{matrix} CH_2-CH_2-CH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H \\ CHMe\cdot CH_2\cdot CH\cdot CO_2H \end{matrix}$, has been obtained.

The diketone was most advantageously oxidised by a cold solution of bromine in aqueous sodium hydroxide. The *acid*, $C_{12}H_{18}O_6$, so obtained was purified by solution in alcohol and addition of chloroform, when the precipitated product was found to contain chloroform (about one mol. of chloroform to two mols. of acid), which could only be completely removed by heating it in a vacuum at the temperature of boiling xylene. The pure acid had m. p. 188°. Its tribasic nature was shown by converting it into the methyl *ester*, $C_{15}H_{24}O_6$, b. p. 200—205°, D^{20} 1·140, n_D 1·47948, $\alpha_D - 27°48'$, by the action of methyl iodide on the *silver* salt. The acid could be recovered unchanged after saponification of the ester.

The same acid was obtained when the diketo-monocarboxylic acid, $C_{14}H_{22}O_4$, was oxidised by bromine in alkaline solution or by nitric acid.　　　　　　　　　　　　　　　　　　　　　　　　H. W.

Studies in the *cyclo*Pentadiene Series. III. Certain Derivatives of 5-Nitro-2 : 3-dibenzoyl-$\Delta^{1,3}$-*cyclo*pentadiene. WILLIAM J. HALE and LAMBERT THORP (*J. Amer. Chem. Soc.*, 1913, 35, 262—272. Compare A., 1912, i, 566; this vol., i, 184).—In the earlier papers, it has been shown that the formation of a *cyclo*-pentadiene ring by the condensation of a 1 : 3-dialdehyde with diphenacyl proceeds more slowly than with acetonylacetone. A study has now been made of the behaviour of pp'-dimethyl-, pp'-dibromo-, and p-bromo-diphenacyl. The results show that the effect of methyl groups in the phenyl rings of diphenacyl is to retard the activity of the methylene groups of this ketone, whilst the presence of bromine atoms increases their activity.

By the condensation of pp'-dimethyldiphenacyl (Limpricht, A., 1900, i, 600) with sodium nitromalonaldehyde, 5-*nitro*-2 : 3-*di-p-toluoyl*-$\Delta^{1,3}$-*cyclo*pentadiene, $NO_2\cdot CH \begin{matrix} CH:C\cdot CO\cdot C_6H_4Me \\ CH:C\cdot CO\cdot C_6H_4Me \end{matrix}$, was obtained in a yield of about 75% of the theoretical; it crystallises in yellow prisms, and decomposes at 243—244°. The *silver* salt decomposes at about 200°, and the *monoxime* at 150—151°.

Ethyl p-bromophenacylbenzoylacetate,
$$\cdot C_6H_4Br\cdot CO\cdot CH_2\cdot CHBz\cdot CO_2Et,$$
m. p. 81°, obtained in 75% of the calculated yield by the condensation of p-bromophenacyl bromide with the sodium derivative of ethyl benzoylacetate, forms colourless needles, and when boiled with dilute potassium hydroxide, is converted into p-*bromodiphenacyl*,
$$CH_2Bz\cdot CH_2\cdot CO\cdot C_6H_4Br,$$

m. p. 116°, which crystallises in white plates with a pearly lustre. The yield of the latter compound amounted to 45% of the theoretical. 5-*Nitro-3-benzoyl-2-p-bromobenzoyl*-Δ¹ ˙-*cyclopentadiene*,

$$NO_2 \cdot CH \Big\langle {}^{CH:C \cdot CO \cdot C_6H_4Br}_{CH:C \cdot CO \cdot C_6H_5} ,$$
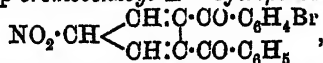
was obtained in a yield of about 75% of the calculated by the condensation of *p*-bromodiphenacyl with nitromalonaldehyde; it forms small, yellow prisms and decomposes at 240—241°.

The *sodium* derivative of *ethyl* p-*bromobenzoylacetoacetate* was prepared by Claisen's method. When the ester itself is warmed with aqueous ammonia, *ethyl* p-*bromobenzoylacetate*,

$$C_6H_4Br \cdot CO \cdot CH_2 \cdot CO_2Et,$$
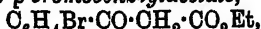
is obtained as a pale yellow, oily liquid which cannot be distilled without decomposition even under 5 mm. pressure. Its sodium derivative condenses with *p* bromophenacyl bromide to form *ethyl* p-*bromobenzoyl-p-bromophenacylacetate*, $C_6H_4Br \cdot CO \cdot CH_2 \cdot CH(CO \cdot C_6H_4Br) \cdot CO_2Et$, m. p. 75°, which crystallises in small, colourless prisms; a 60% yield of the theoretical was obtained. When this ester is boiled with dilute potassium hydroxide, it gives 30% of the calculated yield of *pp'*-dibromodiphenacyl, $C_6H_4Br \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot C_6H_4Br$, m. p. 182°, which forms lustrous, colourless plates, and condenses with nitromalonaldehyde with production of 5-*nitro*-2 : 3-*di*-p bromobenzoyl-Δ¹ ˙-*cyclopentadiene*,

$$NO_2 \cdot CH \Big\langle {}^{CH:C \cdot CO \cdot C_6H_4Br}_{CH:C \cdot CO \cdot C_6H_4Br'}$$
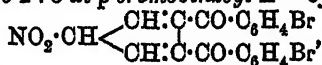
which forms yellow crystals and decomposes at 230—232°.   E. G.

Action of Hydrochloric and Hydrobromic Acids on 2 : 4-Dimethylquinol [2 : 4-Dimethyl-Δ² ⁵-*cyclo*hexadiene-4-ol-1-one]. EUGEN BAMBERGER and EMIL REBER (*Ber.*, 1913, 46, 787—813).—It has been previously shown (Bamberger and Brady, A., 1901, i, 142) that aqueous sulphuric acid converts 2 : 4-dimethyl-Δ³ ⁵-*cyclo*hexadiene-4-ol-1-one into *p*-xyloquinol. Hydrochloric acid, in aqueous solution, transforms it mainly into 5-*chloro*-m-4-*xylenol* and 6-*chloro*-m-4-*xylenol*, whilst, in anhydrous glacial acetic acid solution, the latter isomeride is alone obtained. The actions are probably represented by the scheme:
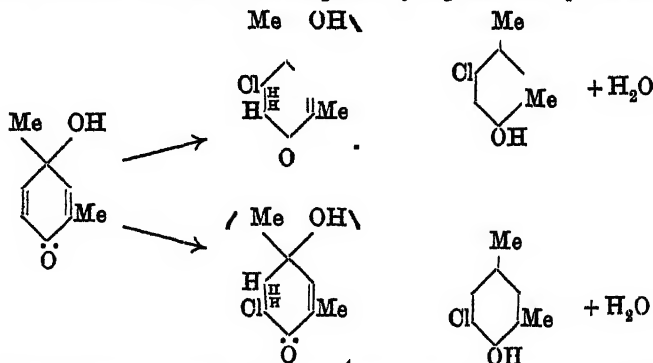
Under similar conditions, hydrobromic acid forms mainly 5-bromo-

m-4-xylenol and 6-bromo-*m*-4-xylenol. The identity of the products was also synthetically established. In the light of the present work, a modified interpretation is given to the observation of Bamberger, Büsdorf, and Szolayski (A., 1899, i, 341) that *p*-nitrosotoluene is converted by hydrochloric and hydrobromic acids into 3-chloro-*p*-cresol, in that hemiquinols are now assumed to be formed as intermediate products.

An improved method for the preparation of 1 : 3-dimethylphenyl-hydroxylamine is described (compare Bamberger and Brady, *loc. cit.*).

2 : 4-Dimethyl-Δ^2 ^{5}-*cyclo*hexadiene-4-ol-1-one was heated during one hour at 100° with fuming hydrochloric acid, the mixture diluted with water, and extracted with ether. After drying the ethereal extract, the ether was removed, the residue was allowed to solidify as completely as possible, the solid portions filtered off, and the liquid part submitted to fractional distillation with steam. The following substances were obtained : 5-chloro-*m*-4-xylenol, b. p. 86·5—87°/9 mm. (*phenylurethane*, m. p. 129—130°; p-*nitrobenzoate*, white needles, m. p. 94—95°); 6-chloro *m*-4-xylenol, white, silky needles, m. p. 90—91° (*benzoate*, glassy prisms, m. p. 84·5—85·5°); a *substance*, m. p. 169—170°, possibly chlorodixylenol; a *substance*, m. p. 190°, reddish-yellow needles, possibly chloro-*p*-xyloquinol; traces of *p*-xyloquinol and resin. In a second experiment, dixylenol was obtained in addition to *p*-xyloquinol and *p*-xyloquinone.

5-Chloro-*m*-4-xylenol was prepared by pouring a diazotised solution of 5-amino-*m*-4-xylenol into boiling cuprous chloride solution, and had b. p. 100—101°/17 mm. The phenylurethane and *p*-nitrobenzoate obtained from it were identical with those obtained above.

The synthesis of 6-chloro-*m*-4-xylenol was effected in the following manner : 6-nitro-*m*-4-xylidine was diazotised and treated with cuprous chloride solution, whereby 4-chloro-6-nitro-*m*-xylene, m. p. 42°, was obtained (compare Ahrens, *Annalen*, 1892, **271**, 17). The latter was reduced by tin and hydrochloric acid to 6-chloro-*m*-4-xylidine, leaflets, m. p. 98·5—99°, which, according to Bamberger and Cadgène (*Dissert.*, 1903), is also formed by the action of concentrated hydrochloric acid on *as*-*m*-xylylhydroxylamine. The *hydrochloride, sulphate,* and *oxalate* were also prepared. The *acetyl* derivative forms silky needles, m. p. 158·5°. *Phenyl-4-chloro*-m-*xylylcarbamide*, $C_6H_2Me_2Cl\cdot NH\cdot CO\cdot NHPh$, white, silky needles, has m. p. 217—218° after previous softening. It immediately re-solidifies, melting again at 255° (decomp.). The corresponding *thiocarbamide* has m. p. 140—140·5° when rapidly heated. When slowly heated it melts at a lower temperature. Diazotisation and subsequent boiling of the aqueous solution converts 6-chloro-*m*-4-xylidine into 6-chloro-*m*-4-xylenol, which is identical with the substance described above.

The action of hydrogen chloride dissolved in glacial acetic acid on 2 : 4 dimethyl*cyclo*hexadienolone gave 6-chloro-*m*-4-xylenol, chloro-*p*-xyloquinol, traces of an oily chloroxylenol, resin, and, possibly, *p*-xyloquinol.

2 : 4-Dimethyl*cyclo*hexadienolone, when heated on the water-bath with aqueous hydrobromic acid, b. p. 122—123°, yielded 5-bromo-*m*-4-xylenol (which possibly contained small quantities of 6-bromo-*m*-4-

xylenol, *as*-m-xylenol, and *p*-xyloquinone), dixylenol, *p*-xyloquinol (or *p*-xyloquinone), and an amorphous *acid*.

To determine the constitution of the above bromoxylenol, it was treated with bromine in glacial acetic acid solution. The *product* obtained, long, white needles, m. p. 179·5—180°, had the same m. p. as 2 : 3 : 6-tribromo-*p*-5-xylenol (obtained by bromination of *p*-xylenol) and 2 : 5 : 6-tribromo-*m* : 4-xylenol (obtained by brominating *m*-xylenol), whilst mixtures of any of the three compounds showed no noticeable depression of m. p. When acted on by benzoyl chloride, however, the *benzoates*, m. p. 151—152°, obtained from 2 : 5 : 6-tribromo-*m* : 4-xylenol, and from the product of the successive action of hydrobromic acid and bromine on 2 : 4-dimethyl*cyclo*hexadienolone, proved to be identical, whereas 2 : 3 : 6-*tribromo*-p-*xylenyl*-5-*benzoate* had m. p. 128—129°; hence, the above monobromoxylenol is probably 5-bromo-*m*-4-xylenol. The *benzoate* and *phenylurethane* of the latter were prepared.

The direct synthesis of 5-bromo *m*-4-xylenol (compare Stoermer and Göhl, A., 1903, i, 848; Orton, Coates, and Burdett, T., 1907, 91, 53) was effected by the action of cuprous bromide solution on a diazotised solution of 5-amino-*m*-4-xylenol hydrobromide. It had b. p. 121 5—122·5°/37 mm., and yielded a benzoate, m. p. 49—50·5°, and a phenylurethane, m. p. 136·5—137°, after previous softening, which proved to be identical with the above-mentioned products.

2 : 4-Dimethyl*cyclo*hexadienolone, when treated with hydrogen bromide in anhydrous glacial acetic acid solution, gave 6-bromo-*m*-4-xylenol, m. p. 76—76·5°, 5-bromo-*m*-4-xylenol, probably *p*-xyloquinone, possibly crude monobromo-*p*-xyloquinol and resin. The constitution of the solid bromoxylenol follows from its identity with the product obtained from 6-nitro-*m*-4-xylidine by conversion of the latter into 4-bromo-6-nitro-*m*-xylene, reduction of this substance by iron filings and acetic acid to 6-bromo-*m*-4-xylidine and diazotisation of the latter substance (compare Noelting, Braun, and Thesmar, A., 1901, i, 589).   H. W.

Preparation of Derivatives of *p*-Benzoquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 253091)—When the dinaphthylamino-*p*-benzoquinones (and their derivatives), obtained by the action of *p*-benzoquinone on α- and β-naphthylamines, are heated with reagents having a high boiling point, they furnish highly coloured compounds, which after sulphonation are of technical importance.

Di - 2 - naphthylaminodichloro-*p*-benzoquinone, $C_6O_2Cl_2(NH \cdot C_{10}H_7)_2$ (obtained from tetrachloro-*p*-benzoquinone and β-naphthylamine), when boiled during three hours with nitrobenzene furnishes the *compound*, $C_{26}H_{15}O_2NCl$, glistening, green crystals, m. p. above 300°, whilst the isomeric *compound* from α-naphthylamine has similar properties.

The *compound*, $C_{52}H_{29}O_4N_4Cl$, is obtained from di-2-naphthylamino-chloro-*p*-benzoquinone, whilst that from di-2-naphthylamino-*p*-benzoquinone, $C_6H_2O_2(NH \cdot C_{10}H_7)_2$, forms a brownish-yellow powder.   F. M. G. M.

Preparation of Chloroanthraquinones. BADISCHE ANILIN-& SODA-FABRIK (D.R.-P. 254450. Compare A., 1908, i, 994, and this vol., i, 49, 61).—The preparation of α-chloroanthraquinones by the replacement of a nitro-group by chlorine has been described (*loc. cit.*), and the reaction has now been extended to the β-nitroanthraquinones.

When a suspension of 2-nitro-3-methylanthraquinone in trichlorobenzene is treated with chlorine at 150—180°, it gives rise to a yellow precipitate consisting of a mixture of ω-2-tetrachloro- and ω-2-trichloro-3-methylanthraquinones, which by the action of hot concentrated sulphuric acid, followed by treatment with sodium carbonate, furnishes a readily separable mixture of 2-*chloroanthraquinone*-3-*carboxylic acid*, m. p. 280°, and of 2-*chloroanthraquinone*-3-*aldehyde*, m. p. 229°, whilst the technical mixture of 1 : 6- and 1 : 7-dinitroanthraquinones give rise on similar treatment to 1 : 6-*dichloroanthraquinone*, $C_{14}H_6O_2Cl_2$, m. p. 202—204°.　　　F. M. G. M.

Preparation of 1-Halogen-2-aminoanthraquinones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 253683. Compare A., 1904, i, 256).—When 2-aminoanthraquinone-3-sulphonic acid is treated with a halogen (1 mol.) it readily yields a 1-halogen-2-aminoanthraquinone-3-sulphonic acid, which by heating with 80% sulphuric acid is converted into the corresponding 1-halogen-2-aminoanthraquinone.

Sodium 1-*chloro*-2-*aminoanthraquinone*-3-*sulphonate* forms orange-red crystals; 1-*chloro*-2-*aminoanthraquinone*, yellow needles, m. p. 228—229°; *sodium* 1-*bromo*-2-*aminoanthraquinone*-3-*sulphonate*, orange-red leaflets, and 1-*bromo*-2-*aminoanthraquinone*, glistening, brownish-red leaflets, m. p. 305°, which on further bromination yields 1 : 3-dibromo-2-aminoanthraquinone.　　　F. M. G. M.

Preparation of Nitro-*p*-acyldiaminoanthraquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D. R.-P. 254185).—Nitro-*p*-acyldiaminoanthraquinones are readily obtained by the action of nitric acid (D 1·5) at temperatures not exceeding 25° on diacyl-1 : 4-diaminoanthraquinones, the nitro-group entering the ortho-position with respect to an amino-group.

2-*Nitro*-1 : 4-*diacetyldiaminoanthraquinone* forms yellowish-brown needles, m. p. 237° (decomp.), and on hydrolysis furnishes 2-*nitro*-1 : 4-diaminoanthraquinone as a blue, crystalline powder.

2-*Nitro*-1 : 4-*diaminoanthraquinoneurethane*, orange-red needles, m. p. 230—232°, is obtained in a similar manner from 1 : 4-diaminoanthraquinoneurethane.　　　F. M. G. M.

Preparation of Dianthraquinonylthio-ethers. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254561).—Dianthraquinonyl thio-ethers are readily prepared by heating anthraquinone mercaptans.

ββ-*Dianthraquinonyl thio-ether*, yellow needles, is thus obtained from anthraquinone β-mercaptan; the isomeric αα-*dianthraquinonyl thio-ether* is a reddish-brown, crystalline powder, whilst αβ-*dianthraquinonyl thio-ether* is prepared by heating together molecular proportions of α- and β-anthraquinone mercaptans.

6-Chloro-1-benzoylaminoanthraquinone when treated with sodium

sulphide furnishes 1-benzoylaminoanthraquinone 6-mercaptan ; this, when heated, gives rise to 1 : 1'-*dibenzoyldiamino*-6 : 6'-*dianthraquinonyl thio-ether*, which crystallises from nitrobenzene in yellow needles.

F. M. G. M.

Anthraflavone-G. EDUARD HEPP, RUDOLF UHLENHUTH, and FRITZ ROMER (*Ber.*, 1913, 46, 709—712).—To the above dye (D.R.-P.199756) has been attributed the structure 1 : 2 : 5 : 6-diphthaloylanthracene (Bohn, A., 1910, i, 405). In its preparation by the action of calcium hydroxide on ω-dichloromethylanthraquinone, the occurrence of large quantities of anthraquinone-2-carboxylic acid as by-product suggests that the first product of the reaction is anthraquinone-2-aldehyde, which then undergoes change into the corresponding acid and alcohol, the latter of which then condenses to anthraflavone. According to this view the dye must be diphthaloylstilbene, and its formation by the action of lead oxide on 2-methylanthraquinone and its derivatives would be analogous to the well-known formation of stilbene from toluene. A convincing proof of the untenability of the older view with regard to the structure is given by the preparation of the dye in better yields than hitherto, from ω-dibromo-2-methylanthraquinone by the action of copper powder or sodium iodide on solutions in nitrobenzene and acetone respectively.

The last method of preparation can be extended to substituted anthraflavones. 1-*Chloro*-2-*methylanthraquinone*, yellow needles, m. p. 171°, obtained from 2-methylanthraquinone-1-sulphonic acid by heating with potassium chlorate and hydrochloric acid, when treated with bromine in nitrobenzene solution is converted into 1-*chloro*-ω-*dibromomethylanthraquinone*, yellow leaflets, m. p. 176° ; the action of sodium iodide on the acetone solution of this substance produces 1 : 1'-*dichloroanthraflavone* (2 : 2'-dichloro-3 : 4 : 3' : 4'-diphthaloylstilbene), a yellow, crystalline powder.

The new formula for this class of dye also gives a satisfactory explanation of other properties, such as the quantitative conversion into the corresponding anthraquinonecarboxylic acids.   D. F. T.

2-Methylanthraquinone. FRITZ ULLMANN AND KARL LUDWIG KLINGENBERG (*Ber.*, 1913, 46, 712—725).—The authors have found that for the preparation of anthraquinone-2-aldehyde in larger quantities, the best method is by the intermediate formation of ω-dibromomethylanthraquinone. The stilbene structure for anthraflavone (see Hepp, Uhlenhuth, and Römer, preceding abstract) is confirmed.

Anthraquinone-2-*aldehyde* can be obtained by the gradual addition of a mixture of chromic acid and acetic acid to a suspension of 2-methylanthraquinone in acetic anhydride containing a little sulphuric acid, and also by heating ω-dibromomethylanthraquinone (prepared by the action of bromine on the methylanthraquinone in nitrobenzene solution at 150—160°) with concentrated sulphuric acid at 125—130°. The aldehyde forms pale yellow leaflets or needles, m. p. 188—189° (corr.) ; *phenylhydrazone*, reddish-violet needles, m. p. 242°(corr.); *oxime*, straw-yellow needles, m. p. 238—239° ; *semicarbazone*, yellow needles, m. p.

397° (corr.); *azine*, yellow needles, m. p. 410°: *sodium disulphite* compound, colourless crystals.

When a suspension of anthraquinone-2-aldehyde in dimethylaniline with zinc chloride is heated on a water-bath, condensation occurs; the same substance, 2-*anthraquinonyltetramethyldiaminodiphenylmethane*, is obtained when ω-dibromomethylanthraquinone is warmed with dimethylaniline and zinc chloride; it crystallises in red needles, m. p. 240—241° (corr), and can be oxidised to a green colouring matter.

The reaction between ω-dibromomethylanthraquinone and dimethylamine or diethylamine follows a different course at the b. p. of the mixture, the product being the same as that from the action of copper powder on dibromomethylanthraquinone, namely, anthraflavone,

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_4 \cdot CH{:}CH \cdot C_6H_4{<}^{CO}_{CO}{>}C_6H_4$$
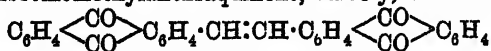
(diphthaloylstilbene, dianthraquinonylethylene), identical with the known dye; it is oxidised by sodium dichromate and nitric acid to anthraquinone-2-carboxylic acid, m. p. 285°, and when boiled with bromine in nitrobenzene solution yields the *dibromide*, m. p. above 400°; this on boiling with diethylaniline regenerates the anthraflavone.

If ω-dibromomethylanthraquinone is heated at 240—250°, hydrogen bromide is eliminated and 2 : 2′-*dianthraquinonylacetylene dibromide*, yellow needles, m. p. 360°, is obtained; when heated with diethylaniline or alkali phenoxide, the last substance is converted into 2 : 2′-*dianthraquinonylacetylene (diphthaloyltolane)*, yellow leaflets, m. p. 350—353°, which unites with bromine to yield the dibromide, and is oxidised by chromic acid in the presence of nitric acid to anthraquinone-2-carboxylic acid; it can also be reduced by hyposulphite to a red vat, which dyes cotton yellow.
                                                                                                D. F. T.

Action of Carbon Dioxide on the Magnesium Compound of Fenchyl Chloride.

GUSTAV KOMPPA and S. V. HINTIKKA (*Ber.*, 1913, **46**, 645—648).—Fenchyl chloride reacts with magnesium in the course of a week, and when carbon dioxide is passed through the product, the reaction leads to as complicated a mixture as Houben experienced in the case of pinene hydrochloride (A., 1893, i, 42). When the ethereal extract is shaken with sodium carbonate it gives, starting from inactive fenchyl chloride, a clear aqueous solution containing hydrofenchenecarboxylic acid and an emulsion from which a small quantity of *hydrodifenchenecarboxylic acid*,

$$C_{10}H_{17} \cdot C_{10}H_{16} \cdot CO_2H,$$
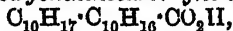
may be isolated in the form of long, glistening needles, m. p. 106°, whilst the predominating, neutral portion, on fractionation, yields an almost inactive *hydrodifenchene*, $C_{20}H_{34}$, as a glycerol-like liquid, b. p. 155—157°/10 mm., D_4^{17} 0·9564, n_D 1·50928, and also inactive fenchene, and probably some fenchyl alcohol.

Active fenchyl chloride, a_D^{18} − 6°0′, however, gives a better yield of *hydrofenchenecarboxylic acid*, $C_{10}H_{17} \cdot CO_2H$, in the form of a white, very soluble, inactive mass, b. p. 140—142°/20 mm., m. p. 52—53°, which yields an *amide*, m. p. 107°, and an *anilide*, m. p. 105—106°. On the other hand, no hydrodifenchenecarboxylic acid is obtained, and less neutral substances are formed, from which active *hydrodifenchene*,

b. p. 155—156°/10 mm., D_1^{17} 0 9652, n_D 1·51299, a_D^{18} +5°30′, and an active fenchene, a_D^{20} +4°17′, have been isolated.   J. C. W.

Preparation of Esters of Dibromo-β-phenylpropionic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254666. Compare this vol., i, 63).—*Fenchyl di bromo-β-phenylpropionate*, colourless, tasteless prisms, m. p. 105°, and of therapeutic value, is readily prepared by heating together fenchyl alcohol and dibromo-β-phenylpropionyl chloride in benzene solution.   F. M. G. M.

Preparation of a Fenchyl Ester. CHEMISCHE FABRIK VON KERESZTY, WOLF & CIE (D.R.-P. 253756).—*Fenchyl salicylate*, m. p. 51°, is of therapeutic value, and can be prepared by known methods from fenchyl alcohol and salicylic acid (or methyl salicylate).
    F. M. G. M.

The Constitution of Camphene. EDUARD BUCHNER and WILHELM WEIGAND (*Ber.*, 1913, 46, 759—768).—Of the three suggested formulæ for camphene :

$$
\begin{array}{ccc}
\text{CH}_2\cdot\text{CH—CMe}_2 & \text{CH}_2\cdot\text{CH—CMe}_2 & \text{CH}_2\text{——CH} \\
| & | \quad | & | \\
\text{CH}_2 & \text{CH}_2 \ \text{CH} & \text{CH}\cdot\text{CMe}_2\text{—}\ \ \text{CMe} \\
| & | \quad \| & | \\
\text{CH}_2\cdot\text{CH—C:CH}_2 & \text{CH}_2\cdot\text{CH—CH} & \text{CH}_2\text{——CH} \\
\text{(I.)} & \text{(II.)} & \text{(III).}
\end{array}
$$
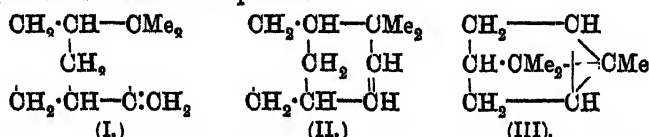
the first (Wagner's formula) has been received with most favour (compare Semmler, A., 1909, i, 170; Harries and Palmén, A., 1910, i, 497; Komppa, A., 1911, i, 388), and has received additional support from molecular refractivity considerations (von Auwers, A., 1912, ii, 214). A final decision on purely chemical grounds appears to be possible by the application of ethyl diazoacetate.

It has already been shown that benzene and ethyl diazoacetate couple with loss of nitrogen to form ethyl norcaradienecarboxylate,

$$\begin{array}{c}\text{CH:CH·CH} \\ \text{CH:CH·CH} \end{array}\!\!>\text{CH·CO}_2\text{H},$$

which after hydrolysis can be oxidised to *cyclo*propane-*trans*-1 : 2 : 3-tricarboxylic acid (Braren and Buchner, A., 1901, i, 385). If this reaction could be applied generally, a substance of formula 1 should yield 2 : 2-dimethylnor-
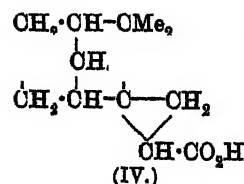
$$
\begin{array}{c}
\text{CH}_2\cdot\text{CH—CMe}_2 \\
| \\
\text{CH}_2 \\
| \\
\text{CH}_2\cdot\text{CH-C—CH}_2 \\
\diagdown\diagup \\
\text{CH·CO}_2\text{H} \\
\text{(IV.)}
\end{array}
$$

camphane-3-*spirocyclo*propanecarboxylic acid (formula IV annexed), which might be oxidised to *cyclo*propane-1 : 1 : 2-tricarboxylic acid ; a substance of formula II would give finally *cyclo*propane-1 : 2 : 3-tricarboxylic acid, whilst a substance of formula III would not react with ethyl diazoacetate. Experiment gives results in entire accord with the first of these possibilities, thus providing apparently final evidence in favour of formula I.

It is interesting to note that the condensation product of ethyl diazoacetate and camphene is a *spirane* molecule with three-ring systems, this view being supported by determinations of the molecular refraction and dispersion.

The camphene used was mainly prepared from bornyl chloride by the action of aniline (Ullmann and Schmid, A., 1911, i, 70); the same condensation product was always obtained. For the condensation, a mixture of 5 grams of camphene with 5 grams of methyl diazoacetate was gradually added to 30 grams of camphene (m. p. 44—45°; b. p. 156—157°/745 mm.; $[a]_D^{15} + 62.59°$) containing 1 gram of copper powder as catalyst, at 160—165°. A practically theoretical volume of nitrogen is liberated, and *methyl* 2 : 2-*dimethylnorcamphane*-3-spirocyclo-*propanecarboxylate* is obtained as a colourless oil, b. p. 126°/14 mm., $[a]_D^{19.5} + 6.79°$, $D_4^{18.5}$ 1.0268, $n_D^{18.3}$ 1.48567, with an odour resembling camphene; in suspension in sodium carbonate solution it is stable towards potassium permanganate. The corresponding *ethyl* ester, obtained by the application of ethyl diazoacetate, has b. p. 128—136°/14 mm. The esters can be hydrolysed to the corresponding acid (formula IV) by alcoholic potassium hydroxide, and the product was purified by conversion into the acid *chloride*, which is changed by concentrated aqueous ammonia into the *amide*, colourless leaflets, m. p. 124°; 2 : 2-*dimethylnorcamphane*-3-spirocyclopropanecarboxylic *acid*, obtained by hydrolysis of this, forms colourless needles, m. p. 108°; the *calcium*, *barium*, *lead*, and *silver* salts were obtained by precipitation from an aqueous solution of the *ammonium* salt. When an intimate mixture of the amide with sodium hypobromite solution is warmed on a water-bath, 2 : 2-*dimethylnorcamphane*-3-spiroaminocyclopropane is produced as an unpleasant smelling oil; *hydrochloride*, colourless leaflets, m. p. 253° (decomp.); yellow *aurichloride*, m. p. 160° (decomp.); *platinichloride*, golden prisms decomposing at 237°; yellow *picrate*, m. p. 201°.

If the methyl ester obtained by the condensation of camphene and methyl diazoacetate is treated in alcoholic solution with sodium, it becomes reduced to 2 : 2-*dimethylnorcamphane*-3-spirocyclopropane-*methylol*, $C_{11}H_{17}\cdot CH_2\cdot OH$, a colourless, viscous liquid, b. p. 129°/12 mm., $a_D^{20} + 26.79°$, D_4^{19} 0.9972, n_D^{19} 1.50205, with an odour resembling that of camphene; *phenylurethane*, needles, m. p. 234°.

The oxidation of 2 : 2-dimethylnorcamphane-3-*spirocyclo*propane-carboxylic acid was effected in dilute sulphuric acid by potassium permanganate, the last substance is added as required, and the process occupies many hours; the oxidation tends to proceed too far, and only a relatively small quantity of *cyclo*propane-1 : 1 : 2-tricarboxylic acid was obtained, which on heating lost carbon dioxide with formation of a mixture of *cyclo*propane-1 : 2-*cis*dicarboxylic acid and the corresponding anhydride; acetyl chloride dehydrated this to the pure anhydride, which was definitely recognisable.   D. F. T.

The Constituents of Ethereal Oils. High-boiling Camphor Oil. FRIEDRICH W. SEMMLER and IRENE ROSENBERG (*Ber.*, 1913, **46**, 768—774).—A more careful investigation of the constituents of the blue-coloured, high-boiling camphor oil (compare Schimmel & Co., A , 1909, i, 816).

The oil was separated by distillation into three fractions, b. p. 130—150°/10 mm., 150—170°/10 mm., and 170—190°/10 mm.

The first fraction contained limene and a little cadinene, which were

identified by their hydrogen chloride additive compounds; limene trihydrochloride, m. p. 79°, has before solidification the following properties. b. p. 177—189°/8 mm., D^{20} 1·0370, n_D 1·50152, $[a]_D \pm 0°$. The presence of three ethylenic linkings in limene was proved by reduction in acetic acid with hydrogen and platinum black to *hexahydrolimene*, an optically inactive liquid, b. p. 123—125°, D^{20} 0·8244, n_D 1·45423. This fraction also contained a sesquiterpene, $C_{15}H_{24}$, b. p. 129—133°, D^{20} 0·9015, n_D 1·50058, $[a]_D + 3°$, for which the name *sesquicamphene* is suggested; although the data suggest a bicyclic diolefinic substance, no solid hydrogen chloride additive compound was obtainable.

The second fraction had as almost sole constituent a sesquiterpene alcohol, $C_{15}H_{26}O$, b. p. 159—162°, D 0·95413, for which the name *sesquicamphenol* is suggested; it was purified by conversion into the sodium alcoholate and regeneration by treatment with water; by heating with potassium hydrogen sulphate at 180° for two hours a molecule of water is eliminated with formation of a *hydrocarbon*, b. p. 125—130°, D^{20} 0·9138, n_D 1·50895, $[a]_D + 50°$, which is probably a reduced naphthalene derivative; no solid hydrochloride was obtainable.

The least volatile fraction consisted chiefly of hydrocarbons, from which small quantities of oxygen compounds were removed by heating with sodium; the purified product, b. p. 180—190°/11 mm., D^{20} 0·9276, n_D 1·51986, $[a]_D + 1°$, is a diterpene, $C_{20}H_{32}$, a class of substance generally absent from ethereal oils. If this crude product is treated in ethereal solution with hydrogen chloride, a *tetrahydrochloride*, thin tablets, m. p. 129—131°, is obtained, from which the hydrocarbon can be regenerated in a purer condition by treating successively with a mixture of sodium acetate and acetic acid and then alcoholic potassium hydroxide; it then has b. p. 177—178°/6 mm., D^{20} 0·8870, n_D 1·50339, $[a]_D \pm 0°$. This monocyclic hydrocarbon, for which the name *a-camphorene* is proposed, is reduced by hydrogen and platinum black to *octahydro-a-camphorene*, $C_{20}H_{40}$, b. p. 174—176°/9 mm., D^{20} 0·8526, n_D 1·46470, $[a]_D \pm 0°$. From the oily residue obtained in the preparation of the tetrahydrochloride, could be regenerated by alcoholic potassium hydroxide a bicyclic isomeride, *β-camphorene*, $C_{20}H_{32}$, b. p. 170—180°/10 mm., D^{20} 0·930, n_D 1·518°, $[a]_D \pm 0°$, which gives no solid additive compound with hydrogen chloride.

The blue colour of all high-boiling fractions of camphor oils is due to such small traces of a coloured substance that no particulars of its composition could be determined.   D. F. T.

Caoutchouc and Guttapercha Resins. G. H. HILLEN (*Arch. Pharm.*, 1913, **251**, 94—121).—Proximate analyses have been made of the resinous portions of various kinds of caoutchouc and allied products.

The resinous portion of "pontianac," "bresk" or "dead Borneo," an inferior "rubber" obtained from the latex of *Dyera costulata*, Hook, was found to contain lupeol acetate, α-amyrin acetate, β-amyrin acetate, and a resen (compare Sack and Tollens, A., 1904, i, 1011; Cohen, A., 1907, i, 211, 230). The formula $C_{26}H_{42}O$ is suggested for lupeol.

The caoutchouc (Ceara rubber) of *Manihot glaziovii*, prepared by the

Lewa process in German East Africa, contains 7% of resin. composed of *iso*cholesterol acetate, a soft resin, and a green, amorphous substance.

Guayule caoutchouc contains 16% of resin, composed of soft resinous material, probably formed by the oxidation of the essential oil contained in the plant, which contains no substances giving the phytosterol reactions (compare Alexander, A., 1911, i, 897).

"Malabuwai guttapercha" from *Alstonia grandifolia*, Miq., contains α-amyrin acetate, β-amyrin acetate, an oily substance, and traces of a yellow resen.

The resin of *Palaquium Gutta* from German New Guinea contains lupeol cinnamate, an oily substance, and a small quantity of a resen.

A table giving the percentages of resin, the appearance of the resins under the microscope, and their reactions with the usual phytosterol reagents for a number of commercial caoutchoucs is provided.

The colour reactions of most of the substances referred to in the paper with phytosterol reagents are tabulated.　　　　T. A. H.

The Viscous Transformation of Caoutchouc. A. VON ROSSEM (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 78—83).—According to Gorter (*Mededeelingen over Rubber*, 1911) the transformation of ordinary caoutchouc into the viscous, glue-like modification under the influence of heat, light, and certain chemical reagents is due to depolymerisation. It is suggested that normal polymerised caoutchouc is under ordinary conditions metastable, and that the formation of the viscous variety simply corresponds with the transition from the metastable to the stable form. In support of this view, Gorter describes experiments which show that if a benzene solution of caoutchouc, prepared and kept in the dark, is mixed with a caoutchouc solution which has been exposed to sunlight for some time, the viscosity of the mixed solution gradually diminishes when the solution is protected from the light by means of red glass. In exactly similar circumstances, the viscosity of the original solution was found to remain constant, and the difference in behaviour is supposed to be due to the "inoculation" of the original solution with the stable modification when this solution is mixed with the insolated solution.

To test this theory, measurements of the viscosity of 1% solutions of caoutchouc have been made, with special reference to the influence of light. After exposure to the light from an arc lamp for some hours, the viscosity is found to have diminished, but the subsequent fall is very slow if the solution is kept in the dark, and does not differ from that exhibited by a portion of the original solution which has not been exposed to the arc light. If diffused daylight is allowed access to the solution, the subsequent fall in the viscosity is very much more rapid.

Similar experiments were made with solutions exposed to the light from a Uviol lamp. The results obtained in both series show that there is no after-effect of the light in so far as the viscosity of the solutions is concerned. In some of these experiments the caoutchouc solutions were exposed to the Uviol lamp in glass vessels, whilst in others, quartz vessels were employed. After six and three-quarter

d d 2

hours' exposure, the time of out-flow of a certain volume of solution was found in a particular case to have fallen from 560 to 412 seconds with the glass apparatus, whilst the time required by the solution after exposure in the quartz tube was only 56 seconds. These results indicate that the active rays are the short-waved rays which are absorbed by glass.   H. M. D.

The Hydrohaloids of Artificial and Natural Caout-choucs, and the Caoutchouc-like Substances Regenerated from Them. CARL D. HARRIES (*Ber.*, 1913, **46**, 733—743).— Contrary to the statement of Weber (A., 1900, i, 353), caoutchouc forms additive compounds with hydrogen bromide and hydrogen iodide, as well as with hydrogen chloride. The method followed was to saturate the chloroform solution of the caoutchouc with the gas, and then after several hours to precipitate by alcohol.

Natural caoutchouc unites with two molecules of each acid, forming substances : $C_{10}H_{18}Cl_2$, $C_{10}H_{18}Br_2$, $C_{10}H_{18}I_2$; guttapercha, caoutchouc obtained by the polymerisation of isoprene under the influence of heat and of sodium, and also caoutchouc obtained from dimethylbutadiene, behave in a similar manner, except that the additive compounds of the two former synthetic caoutchoucs with hydrogen iodide, after precipitation, contain only one molecule of hydrogen iodide.

The halogen hydride is only partly removed by treatment with organic bases, but pyridine and piperidine at 125—145° act on the compounds, if necessary in benzene solution, with elimination of the two molecules of hydracid. The products are not identical with natural caoutchouc, but resemble more the synthetic substance obtained by the action of sodium (Harries, A., 1911, i, 798). The elimination of halogen hydride by heating with sodium hydroxide or sodium amide gives a halogen-free caoutchouc, which, however, is apparently different from the natural product and from that obtained by polymeri-sation with sodium. The dihydrochloride of guttapercha, when treated for the elimination of two molecules of hydracid, yields a compound resembling caoutchouc, possibly indicating a conversion of guttapercha into caoutchouc.

From a consideration of the difficulty with which the above new forms of caoutchouc undergo ozonisation, it is tentatively suggested that their molecules include a conjugated pair of ethylenic linkings,

for example, $CHMe\begin{smallmatrix}CH_2 \cdot CH_2 \cdot CH_2 \\ CH:CH——CH\end{smallmatrix}CMe$ and

$$CHMe\begin{smallmatrix}CH_2—CH:CH \\ CH_2 \cdot CH_2 \cdot CH\end{smallmatrix}CMe,$$
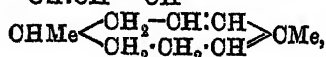
whilst the arrangement in natural caoutchouc is

$$CMe\begin{smallmatrix}CH \cdot CH_2—CH_2 \\ CH_2 \cdot CH_2 \cdot CH\end{smallmatrix}CMe.$$
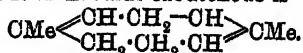
[With EWALD FONROBERT.]—From natural caoutchouc were prepared the dihydrochloride, *dihydrobromide*, and *dihydriodide*; from caoutchouc, obtained by polymerisation on warming, were prepared a *dihydro-chloride*, *dihydrobromide*, and a *hydriodide* ; "sodium polymerised" caoutchouc yielded a *dihydrochloride*, a *hydrobromide*, and a *hydriodide*; "dimethylbutadiene" caoutchouc yielded a *dihydrochloride*, *dihydro-*

bromide, and a *dihydriodide*; guttapercha yielded a *dihydrochloride*, *dihydrobromide*, and a *dihydriodide*. Although affected by hydrofluoric acid no hydrofluoride was obtainable from any of the preceding hydrocarbon substances. The above hydrohaloids are amorphous, sometimes viscous, substances, which undergo decomposition at temperatures between 100° and 200°.

The caoutchouc regenerated from the dihydrochlorides by treatment with pyridine or piperidine at 125—135° resembles "sodium isoprene" caoutchouc in solubility and slow absorption of ozone to produce a diozonide, but yields a relatively stable *dihydrobromide* and *dihydriodide*.

D. F. T.

Theory of Vulcanisation. DAVID SPENCE (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 84—85).—Polemical against Kindscher and Hinrichsen (A., 1912, i, 1007) and Ostwald (A., 1912, i, 706).

H. M. D.

α- and β-Antiarin and on Crystallised Albumin from Antiaris Latex. HEINRICH KILIANI (*Ber.*, 1913, **46**, 667—680. Compare A., 1897, i, 91, and A., 1911, i, 138).—Crystallised rhamnose, m. p. 93—94°, and antiarigenin, m. p. 188°, have been obtained from β-antiarin by means of dilute hydrochloric acid. The α- and β-antiarins only differ in their sugars, and careful analyses lead to the formulæ $C_{27}H_{40}O_{10}, 4H_2O$ and $C_{27}H_{40}O_{10}, 3H_2O$ respectively, whilst antiarigenin receives the formula $C_{21}H_{28}O_5$. The hydrolysis of these glucosides by means of dilute acids is accompanied by the extensive formation of resinous matter, which seems to indicate the presence of a labile aldehyde or ketone group in antiarigenin. The action of the common moulds is quite unavailing, although the glucosides soon disappear from unpreserved antiaris latex, which may, therefore, contain a specific enzyme.

Antiarose could not be obtained crystalline, but the lactone of antiaronic acid, well-defined monoclinic crystals of the epidote type, has been converted into the following derivatives, which differ from those of the known metameric acids: *phenylhydrazone*, long needles, m. p. 143—145°; *quinine* salt, very slender needles, m. p. 180—181°, more soluble in cold water than the *quinine* salt of rhamnonic acid, which forms nodules of silky needles, m. p. 180—182°; *brucine* salt, small, pointed needles with $2H_2O$, m. p. 118—119°; brucine salt of rhamnonic acid, large crystals with $7H_2O$, m. p. 120—126°.

α-Antiarin is considerably attacked by sodium amalgam, and forms an *oxime*, $C_{27}H_{41}O_{10}N, 2H_2O$, m. p. 239—240°, which, however, like the parent substance, is unaffected by aluminium amalgam in the cold. Antiarigenin yields a *semicarbazone*, $C_{22}H_{31}O_5N_3$, which begins to sinter at 225°.

Attempts to oxidise the glucosides with silver oxide or hydrogen peroxide were without result, but the action of chromic acid, nitric acid, or permanganate promises to throw light on their constitution.

"Antiaris residue," the portion of the latex which is insoluble in alcohol, contains a protein which may be extracted to the extent of 6·3% by means of 0·8% acetic acid (compare Kotake and Knoop,

A., 1912, ii, 81). It may be recrystallised from hot 10% acetic acid in the form of white, hygroscopic crystals, which darken at 250°, $[a]_D - 15·2°$. The substance may be titrated, using phenolphthalein, but it could not be shown that the magnesium which accompanies the crude protein is combined as a salt.   J. O. W.

Anthocyanin. III. An Anthocyanin-like Oxidation Product of Euxanthone. MAXIMILIAN NIERENSTEIN (*Ber.*, 1913, **46**, 649—650. Compare A., 1912, i, 42, 292).—When euxanthone (2 : 8-hydroxyxanthone) (I), which is obtained by treating Indian-yellow with hydrochloric acid and ammonia, is oxidised by chromic acid in glacial acetic acid, 2-*hydroxy*-5 : 8-*quinoxanthone* (II) is formed in small, sparkling, deep red needles, which give a blue solution in alkalis and a red in concentrated sulphuric acid. On reduction with zinc dust in acetic anhydride suspension, an amorphous product is obtained, which, on hydrolysis, yields 2 : 5 : 8-*trihydroxyxanthone* (III) in small, light yellow, silky needles with $2H_2O$, m. p. 328—330°. This compound, like its isomeride, gentisein, gives a blood-red colour with sodium amalgam, and its alcoholic solution dyes mordanted cotton. It forms a *triacetyl* derivative, $C_{19}H_{14}O_8$, in faintly yellow needles, m. p. 226—230°, and with diazomethane a *trimethoxyxanthone*, $C_{16}H_{14}O_5$, in pale yellow needles, m. p. 194—195°.

(I.)   (II.)   (III.)
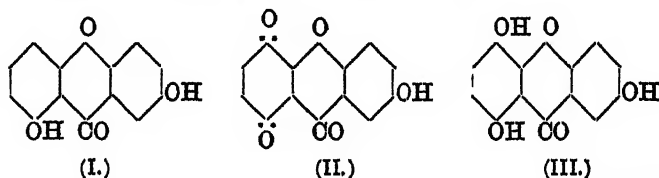
J. O. W.

Action of Sodium Methoxide on Bilirubic Acid, Bilirubin, and Hemibilirubin. HANS FISCHER and HEINRICH ROSE (*Ber.*, 1913, **46**, 439—442).—Bilirubin and hemibilirubin resemble the earlier examined pyrrole derivatives (this vol., i, 71, Fischer and Bartholomäus, this vol., i, 209) in their behaviour towards sodium methoxide at elevated temperatures. When heated with sodium methoxide in alcoholic solution at 220—230°, each gives rise to 2 : 4 : 5-trimethyl-pyrrole-3-propionic acid (identified by the picrate ; compare Fischer and Bartholomäus, *loc. cit.*), together with a little xanthobilirubic acid (see below).

Bilirubic acid under similar treatment gives in good yield an acid *substance*, yellow prisms, m. p. 274°, for which the name *xanthobilirubic acid* (or *xanthopyrrolecarboxylic acid*) is proposed ; *sodium* salt sparingly soluble. It is possible that the acid is the pure form of the dehydrobilic acid of Piloty and Thannhauser (A., 1912, i, 925). On reduction by a mixture of hydriodic and acetic acids it is reconverted into bilirubic acid.

The above results must be regarded as a proof of the presence of a third pyrrole ring in bilirubin and hemibilirubin.   D. F. T.

The Identity of Baphinitone with Homopterocarpin. Hugh Ryan and R. Fitzgerald (*Proc. Roy. Irish Acad.*, 1913, 30, 106—108).—Baphinitone, $C_{17}H_{16}O_4$, obtained from barwood, forms colourless, acicular crystals, m. p. 84° (Anderson, T., 1876, ii, 582, gives m. p. about 88°, and formula $C_{26}H_{26}O_6$). In 4% solution in chloroform it has $[a]_D^{20} - 211·7°$. Similarly, homopterocarpin, obtained from santalin by the method of Cazeneuve and Hugounenq (A, 1887, 971; 1889, 160), was found to melt at 84° (Brooks, A., 1911, i, 154, gives 86°), and to have $[a]_D^{20} - 211°$ in 4% solution in chloroform. In appearance, solubility and m. p., homopterocarpin is identical with baphinitone, and a mixture of the two substances melts at the same temperature as each of its constituents.

A solution of homopterocarpin in chloroform reacts readily with bromine in bright sunlight with the formation of a *substance*, $C_{17}H_{14}Br_2O_4$, colourless needles, m. p. 200°, and of a yellow, amorphous *solid*. Contrary to Cazeneuve's statement, homopterocarpin does not yield methyl iodide when treated with hydriodic acid, and thus contains no methoxy-group; nevertheless, a phenolic substance is obtained by the action of hydriodic acid on it.　　　　　　　H. W.

Optical Activity of Tannin. Emanuel Navassart (*Zeitsch. Chem. Ind. Kolloide*, 1913, 12, 97—99).—The rotatory power of tannin solutions has been examined with reference to the influence of concentration. In the case of aqueous solutions, the rotatory power varies very considerably with the concentration, the value of $[a]_D^{20}$ increasing from 49·8° to 89·7° when the concentration falls from 20% to 0·08%. When dissolved in ethyl alcohol, acetone, and acetic acid, the rotatory power of tannin is much smaller, and varies less with the concentration. For concentrations between 1% and 20%, the observed values of $[a]_D^{20}$ vary from 12·7° to 16·9° in alcohol, from 12·9° to 15·1° in acetone, and from 9·4° to 14·5° in acetic acid. These results seem to show that the rotatory power of the tannin increases as the degree of dispersity of the substance in the various solvents diminishes.

　　　　　　　　　　　　　　　　　　　　　　　H. M. D.

[Preparation of Derivatives of Benzanthrone Containing Sulphur.] Gesellschaft für Chemische Industrie (D.R.-P. 254098). —The action of chlorine (or chlorinating reagents) on 2-methylbenzanthrone (m. p. 199°) gives rise to *chloromethylbenzanthrone*, m. p. 175°; this, when heated with sulphur or polysulphides during two hours at 200—240°, yields the *compound* (annexed formula), glistening, coppery needles.
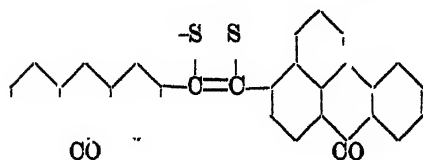
The preparation of *bromomethylbenzanthrone, dichloro-2-methylbenzanthrone*, and of *nitro-* and *amino-benzanthrone* with their sulphur derivatives is also described.　　　　　　　F. M. G. M.

Preparation of Homologues of Hydroquinine. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 254712. Compare A., 1892, 1253).—The alkylation of hydrocupreine has furnished the following derivatives : *Ethylhydrocupreine*, $C_{21}H_{28}O_2N_2$, is amorphous, but its *sulphate* forms colourless needles, whilst *propylhydrocupreine*, $C_{22}H_{30}O_2N_2$, colourless crystals, has m. p. 142°.   F. M. G. M.

Alkaloids of Javanese Coca [Erythroxylon novogranatense]. ANNE W. K. DE JONG (*Rec. trav. chim.*, 1911, 30, 204—210 ; 1912, 31, 249—259. Compare A , 1906, ii, 315).—The method of analysis previously described has been slightly modified, since it is found that the insoluble barium salts, obtained by heating the alkaloids with barium hydroxide, contain small quantities of barium cinnamate in addition to barium β-truxillate. The cinnamic acid is recovered by agitating the mixed acids with chloroform. The mixed acids obtained from the soluble barium salts are also treated with chloroform, when α-truxillic acid, possibly containing also the β-isomeride, remains. The acids obtained from the chloroform solution were found to contain about 50·3% cinnamic acid and 37 9% benzoic acid.

A second specimen of mixed acids was obtained by decomposing the alkaloids by means of hot hydrochloric acid and solution of the product in ether, which left a small residue of impurities. The ethereal solution was shaken with potassium hydroxide, the latter acidified with hydrochloric acid, and again treated with ether, whereby a small quantity of α-truxillic acid remained undissolved. The ethereal solution was evaporated to dryness, and the residue extracted with chloroform, which left a small residue consisting of a mixture of α- and β truxillic acids. The acids obtained from the chloroform solution contained 52·1% cinnamic acid, and 34% benzoic acid mixed with acids of higher molecular weight or with neutral substances.

In the second paper the author has worked out a process for the separation of the acids obtained by the decomposition of the alkaloids of Javanese coca, and has ascertained the presence of the following substances in a specimen of these acids : cinnamic, benzoic, *allo*cinnamic, α-truxillic, β-truxillic and δ-truxillic acids, resinous acids, and neutral substances, together with an acid, m. p. about 150° (probably identical with protococaic acid obtained by Hesse, A., 1903, i, 192), and an acid, m. p. about 190°, possibly identical with β-cocaic acid.

The properties of the truxillic acids and their salts have been investigated. The former are insoluble in light petroleum, but are dissolved in the presence of benzoic or cinnamic acids, the solubility of the α- and γ-acids being, however, only slightly affected. α-, β-, and γ-Truxillic acids are only sparingly soluble in chloroform at the ordinary temperature. Hot chloroform dissolves the β-acid, particularly in the presence of benzoic and cinnamic acids. The δ-acid is soluble in chloroform. The α- and γ-acids are insoluble in benzene, whereas the β- and δ-acids are more soluble in the hot than in the cold solvent. The latter acids may be crystallised from boiling water, in which the α- and γ-acids are but slightly soluble.

One hundred c.c. of an aqueous solution of barium β-truxillate, saturated at 26°, contain 0·028 gram of the salt.

The following salts are sparingly soluble in water : the zinc, cadmium, iron, lead, copper, mercury, and silver salts of the α-acid ; the calcium, barium, strontium, zinc, cadmium, manganese, iron, cobalt, nickel, lead, copper, mercury, and silver salts of the β-acid ; the lead, copper, mercury, and silver salts of the γ-acid ; the same salts of the δ- as of the β-acid, and in addition the magnesium salt. The magnesium salt of the β-acid is soluble in water.　　　　　　　　　　H. W.

Preparation of Therapeutically Valuable Double Salts from Morphine and Narcotine. C. F. BOEHRINGER & SOEHNE (D.R.-P. 254502).—The following therapeutically valuable double salts are readily obtained by treating a hot alcoholic solution of the acid with the requisite amount of the other components. *Morphine narcotine meconate*, $C_7H_4O_7,C_{17}H_{19}O_3N,C_{22}H_{23}O_7N,4H_2O$. *Morphine dinarcotine benzenetrisulphonate*, $C_6H_3(SO_3H)_3,C_{17}H_{19}O_3N,(C_{22}H_{23}O_7N)_2,2H_2O$. *Morphine narcotine phenoldisulphonate,*

$$OH\cdot C_6H_3(SO_3H)_2,C_{17}H_{19}O_3N,C_{22}H_{23}O_7N,2H_2O.$$
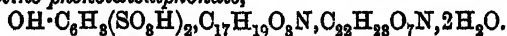
Morphine dinarcotine disulphosalicylate,

$$OH\cdot C_6H_3(SO_3H)_2\cdot CO_2H,C_{17}H_{19}O_3N,(C_{22}H_{23}O_7N)_2,H_2O.$$
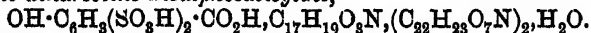
Dimorphine narcotine disulphosalicylate,

$$OH\cdot C_6H_3(SO_3H)_2\cdot CO_2H,(C_{17}H_{19}O_3N)_2 C_{22}H_{23}O_7N,2H_2O.$$
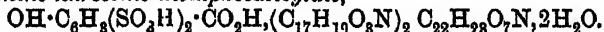
Morphine narcotine sulphate, $H_2SO_4,C_{17}H_{19}O_3N,C_{22}H_{23}O_7N,4\tfrac{1}{2}H_2O$. They form colourless crystals, sparingly soluble in cold, readily in hot water, and somewhat insoluble in the ordinary organic media.

F. M. G. M.

Preparation of Morphine Esters of Alkyl- and Aryloxy-fatty Acids. CHEMISCHE FABRIK VON FRIEDR HEYDEN (D.R.-P. 254094).—*Diethoxyacetylmorphine*, an oil, is prepared by heating morphine (10 parts) with ethoxyacetic anhydride (37 parts) during several hours at 40—45° ; the *hydrochloride*, glistening leaflets, decomposes at about 142°.

Ethoxyacetylmorphine, m. p. 155° (about), is obtained accompanied by the foregoing compound when the proportions of the reacting components are varied, and the mixture heated at 40—50° ; the *hydrochloride,* needles, has m. p. 183—186°. *Diphenoxyacetylmorphine,* m. p. 125° (decomp.), faintly-coloured crystals, is prepared in an analogous manner.　　　　　　　　　　　　　　　　F. M. G. M.

Alkaloids of Pareira Root. MAX SCHOLTZ (*Arch. Pharm.*, 1913, **251**, 136—151. Compare A., 1913, i, 87, and Faltis, 1912, i, 796).—As the result of further analyses, the author now reverts to the formula $C_{18}H_{21}O_3N$, which he used originally for the bebeerines. Bebeerine, *iso*-bebeerine, and β-bebeerine can all be represented by the extended formula $OH\cdot C_{16}H_{14}O(OMe):NMe$. The first and third isomerides yield with acetic anhydride the same optically inactive hydroxytriacetylbebeerine. The latter appears to be formed by the opening of a ring containing nitrogen, the attachment of an acetyl group to the N-atom, and of the residue $CH_3\cdot CO\cdot O$ to the carbon atom formerly linked to the N-atom.

*iso*Bebeerine yields two hydroxytriacetyl*iso*bebeerines, one dextro-rotatory and the other inactive.

*iso*Bebeerine, $C_{18}H_{21}O_3N$, m. p. 297° (decomp.), is the chief constituent of "crystallised bebeerine sulphate" (Merck); the *hydriodide*, m. p. 300° (approx. decomp.), forms prisms from water; the *hydrochloride* is precipitated as colourless needles on adding hydrochloric acid to a solution of the sulphate; the *methiodide*, B,MeI, m. p. 275° (decomp.), forms large, prismatic crystals containing water of crystallisation. On heating with acetic anhydride, *iso*bebeerine yields (1) *α-hydroxy-triacetyl*isobebeerine, m. p. 130—140°, $[a]_D^{20} + 68·1°$ in pyridine, which is colourless and amorphous, and *β-hydroxytriacetyl*isobebeerine, m. p. 291° (approx.), $[a]_D = 0°$, which crystallises in colourless needles and is only soluble in pyridine. On hydrolysis by sodium hydroxide in alcohol, each triacetyl derivative yields a corresponding *hydroxymono-acetyl*isobebeerine; the α-compound, m. p. 280° (approx.), crystallises in colourless, slender needles, and the β-isomeride, m. p. 332° (approx.), forms microscopic needles. Both are insoluble, except in solutions of the alkali hydroxides. *Benzoyl*isobebeerine, m. p. 215° (approx.), obtained by the action of benzoic anhydride on *iso*bebeerine, crystallises from alcohol in glancing, yellow leaflets.

β-Bebeerine, $C_{18}H_{21}O_3N$, is amorphous, but yields a crystalline *methiodide*, B,MeI, m. p. 80° (hydrated) or 258—259° (dry, decomp.). Both bebeerine and β-bebeerine on heating with acetic anhydride yield the same *hydroxytriacetylbebeerine*, $C_{24}H_{29}O_7N$, m. p. 125—135°, which is amorphous, and loses two acetyl groups on treatment with potassium hydroxide in alcohol.   T. A. H.

Zygadenine, the Crystalline Alkaloid of Zygadenus inter-medius. FREDERICK W. HEYL, F. E. HEPNER, and SYLVESTER K. LOY (*J. Amer. Chem. Soc.*, 1913, **35**, 258—262).—It has been shown already (A., 1911, ii, 325) that the leaves of *Zygadenus intermedius* yield 0·3—0·4% of a mixture of alkaloids. Further work on this subject has resulted in the isolation of a pure alkaloid, *zygadenine*, $C_{39}H_{63}O_{10}N$, m. p. 200—201°, $[a]_D - 48·2°$, which crystallises from benzene in clusters of lustrous needles, and from alcohol in ortho-rhombic prisms containing 2Et·OH; the *aurichloride* forms long, dense prisms. The alkaloid gives a yellowish-orange coloration with concentrated sulphuric acid, changing to a brilliant cherry-red. Its physiological action resembles that of veratrine.   E. G.

Electrochemical Reductions. III. Reduction of Nitroso-amines. HILMAR JOHANNES BACKER (*Rec. trav. chim.*, 1913, **32**, 39—47. Compare A., 1912, i, 339, 730).—Nitrosopiperidine suspended in sulphuric acid (10%) was electrolysed at a cathode of tinned copper when an 81% yield of the corresponding hydrazine (estimated by oxidation to the tetrazone) was obtained (compare Knorr, A., 1884, 467; Ahrens, A., 1897, i, 369). At a platinum electrode, the hydrogen was incompletely utilised, and the yield of hydrazine sank to 32%. An excess of hydrogen was found to be practically without effect on the hydrazine.

Diaminopiperazine was obtained in 55% yield by the action of zinc

dust and acetic acid on dinitrosopiperazine (compare Schmidt and Wichmann, A., 1892, 210). Electrolytic reduction at a tinned copper cathode of a suspension of the latter in a mixture of acetic and sulphuric acids gave a 38% yield of diaminopiperazine, which, however, increased to 72% when the mixture of acids was replaced by an aqueous solution of sodium sulphate to which a few drops of sulphuric acid had been added. An attempt to convert dinitrosopiperazine into dinitropiperazine by the action of nitric acid was unsuccessful.

Phenylmethylhydrazine (compare Fischer, A., 1878, 312; 1887, 138) was formed by electrolytic reduction of phenylmethylnitrosoamine suspended in dilute acetic acid at a tinned copper cathode. The yield was 79% of the theoretical.

α-Nitroso-α-methylcarbamide, $NH_2 \cdot CO \cdot NMe \cdot NO$, was readily reduced in sulphuric acid suspension at a tin cathode with the formation of methylsemicarbazide (compare Brüning, A., 1890, 23; Young and Oates, T., 1901, 79, 662), which was identified by conversion into benzylidenemethylsemicarbazone, white needles, m. p. 163°. Young and Oates (loc. cit.) give 159—160° as m. p. of this substance, whilst Michaelis and Hadanck (A., 1908, i, 1020) found 162°.   H. W.

Indole. RUDOLF WEISSGERBER (Ber., 1913, 46, 651—659).—The difficulty experienced in preparing derivatives of indole is chiefly due to the lability of the imino-hydrogen atom. If this atom is replaced by a group which can be subsequently removed, it is found possible to obtain halogen derivatives by direct substitution and to disrupt the indole ring so that anthranilic acid results.

[With ARNO KLEMM.]—Halogens react violently with indole, and only by working in very dilute solutions could Pauly and Gundermann obtain iodoindole (A., 1909, i, 71). When 1-benzoylindole (A., 1911, i, 155), however, is treated in the cold with bromine in carbon disulphide, bromo-1-benzoylindole, $C_{15}H_{10}ONBr$, is obtained in thick plates, m. p. 97—98°, which may be hydrolysed by dilute ammonia or, more conveniently, by means of sodium ethoxide in alcoholic solution, when water precipitates bromoindole, C_8H_6NBr, in silvery leaflets which have a strong fœcal odour and undergo vigorous decomposition at 67°. The compound is not very stable, but the bromine atom resists the action of alkalis.

1-Benzoylindole also combines with chlorine, and the chloro-1-benzoylindole, colourless prisms, m.p. 97—99°, may be hydrolysed to the chloroindole which Mazzara and Borgo obtained by the action of sulphuryl chloride on indole (A., 1906, i, 304). Since the benzoyl derivatives may be oxidised to benzoylanthranilic acid, the halogen is present in the pyrrole ring, and, from their similarity to Pauly's 3-iodo-indole, the constitution of which was satisfactorily determined, the conclusion is drawn that the bromo- and chloro-derivatives are also substituted in position 3, although all three compounds give 2-oxindole when treated with dilute acids.

[With O. HERZ.]—The oxidation of indole itself results in the formation of amorphous masses, but the benzoyl compound is readily converted by permanganate in acetone solution into benzoylanthranilic acid, and this, by hydrolysis, into anthranilic acid itself.

[With F. Kraft.]—The conversion of an indole derivative into indigotin has been accomplished by passing ozone through a strongly alkaline solution of 3-indolecarboxylic acid (A., 1911, i, 155). The reaction commences quickly, but the yield is only about 38%, anthranilic acid being isolated from the by-products. Other oxidising agents do not yield indigotin, neither does 2-indolecarboxylic acid give rise to that dye. J. C. W.

Preparation of Substituted Indoles by the Catalytic Decomposition of Hydrazones. ALEXANDER E. ARBUZOV and V. M. TICHVINSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 70—74).— When heated with cuprous chloride or bromide, or platinous or zinc chloride, hydrazones of aldehydes and ketones undergo catalytic decompositions in directions depending on their structures and on the magnitudes of the radicles present. In the cases already investigated, the principal products are substituted indole derivatives.

Methyl-ethyl-ketone-phenylhydrazone (50 grams), when heated at 180—230° in presence of cuprous chloride (0·1 gram), yields 2 : 3-dimethylindole, the yield being about 60%.

Similarly, propaldehydephenylhydrazone gives skatole in 73—74% yield, whilst propaldehydetolylhydrazone gives 3 : 5-dimethylindole, $C_{10}H_{11}N$, which crystallises in feathery masses of colourless, silky needles, m. p. 74—74·5°. T. H. P.

5-, 6-, and 8-Iodoquinolines and Their Derivatives. JOHANN HOWITZ, HEDWIG FRAENKEL, and ELSE SCHROEDER (*Annalen*, 1913, **396**, 53—75).—8-Aminoquinoline is obtained by the reduction of 8-nitroquinoline best by iron and acetic acid. When tin or stannous chloride and hydrochloric acid are used, the resulting 8-aminoquinoline is contaminated with 5-chloro-8-aminoquinoline. 8-*Iodoquinoline*, C_9NH_6I, m. p. 36°, colourless needles, prepared from diazotised 8-aminoquinoline in the usual manner, forms a *platinichloride*,

$$2C_9NH_6I,H_2PtCl_6,2H_2O,$$
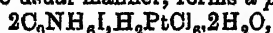
m. p. 251°, orange needles, and *methiodide*, m. p. 200°, yellow needles. By oxidation with alkaline potassium ferricyanide, the latter yields

8-*iodo*-1-*methyl*-2-*quinolone*, $C_9H_3I<^{NMe\cdot CO}_{CH=CH}$, m. p. 168°.

The 8-iodoquinoline, m. p. 136°, described by Claus and Grau in 1893, is 5-chloro-8-iodoquinoline, produced from the impure 8-amino-quinoline mentioned above.

8-Iodoquinoline is readily nitrated by concentrated sulphuric acid and nitric acid (D 1·5) in the cold, yielding 8-*iodo*-5-*nitroquinoline*, m. p. 192°, pale yellow needles. 8-*Iodo*-5-*aminoquinoline*,

$$C_9NH_5I\cdot NH_2,H_2O,$$
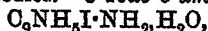
m. p. 148° (anhydrous, 155°), brown prisms (*benzoyl* derivative,

$$C_{16}H_{11}ON_2I,H_2O,$$
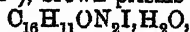
m. p. 218°, leaflets), yields 5 : 8-*di-iodoquinoline*, m. p. 162°, and 5-*chloro*-8-*iodoquinoline*, m. p. 138°, by the usual methods.

By the Sandmeyer process, 5-aminoquinoline yields 5-chloroquinoline, m. p. 44—45° (Claus and Junghanns give 31°), the nitration of which

produces 5-chloro-8-nitroquinoline, m. p. 136° (184°, Claus and Junghanns). 5-Chloro-8-aminoquinoline, m. p. 75° (69°, Claus and Junghanns), forms an *acetyl* derivative, m. p. 140°, and is converted into 5-chloro-8-iodoquinoline by the usual method.

8-Iodoquinoline is readily attacked by 40% fuming sulphuric acid in the cold, yielding 8-*iodoquinoline-5-sulphonic acid*, $C_9NH_5I\cdot SO_3H$, silver-grey leaflets, of which the *sodium* and *barium* salts are described. The *silver* salt, $C_9NH_5I\cdot SO_3Ag,\frac{1}{2}H_2O$, when dehydrated, reacts with methyl iodide at 120—130° to form chiefly the *betaine*, m. p. 292° (decomp.), of 8-iodo-1-methylquinoline-5-sulphonic acid, and with ethyl iodide at 130—140° to form *ethyl 8-iodoquinoline-5-sulphonate*,

$$C_9NH_5I\cdot SO_3Et,$$
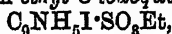
m. p. 156°, colourless leaflets, and the *betaine*, m. p. about 340° (decomp.), of 8-iodo-1-ethylquinoline-5-sulphonic acid. Sodium 8-iodo-quinoline-5-sulphonate and phosphorus pentachloride at 125—130° yield 8-*iodoquinoline-5-sulphonyl chloride*, m. p. 116°, yellow needles or prisms, from an ethereal solution of which and dry ammonia the *sulphonamide*, $C_9NH_5I\cdot SO_2\cdot NH_2$, m. p. 212°, is obtained. The position of the sulpho-group in 8-iodoquinoline-5-sulphonic acid is proved by nitration, whereby the sulpho- is replaced by the nitro-group, and 8-iodo-5-nitroquinoline, m. p. 192°, is obtained.

5-Iodoquinoline methiodide is oxidised to 5-*iodo-1-methyl-2-quinolone*, m. p. 172°, yellow leaflets, by alkaline potassium ferricyanide. 5-*Iodo* 8-*nitroquinoline*, m. p. 160°, yellow needles, obtained by the nitration of 5-iodoquinoline on the water-bath, yields by reduction 5-*iodo-8-aminoquinoline*, m. p. 122°, brown needles (*benzoyl* derivative, m. p. 161°), from which 5 : 8-di-iodoquinoline, m. p. 161°, and 8-*chloro-5-iodoquinoline*, m. p. 118°, are prepared by the usual methods; the formation of the di-iodo-compound determines the orientation of the nitro-group in nitrated 5-iodoquinoline.

The following derivatives of 6-iodoquinoline have been prepared: 6-*Iodo-1-methyl-2-quinolone*, $C_{10}H_8ONI$, m. p. 129°, yellow needles or leaflets; 6-*iodo-5-aminoquinoline*, m. p. 176° (*acetyl* derivative,

$$C_{11}H_9ON_2I,H_2O,$$
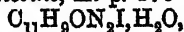
m. p. 197°); 5 : 6-*di-iodoquinoline*, m. p. 125°, and 5-*chloro-6-iodo-quinoline*, m. p. 141°. C. S.

2-*op*-Dinitrophenyl*iso*quinolinium Chloride and its Products of Transformation. THEODOR ZINCKE and G. WEISSPFENNING (*Annalen*, 1913, **396**, 103—131).—The authors' experiments have not realised their expectations that the action of arylamines or of cyanogen bromide on 2-*op*-dinitrophenyl*iso*quinolinium chloride would yield the glutacondialdehyde derivative, $CHO\cdot C_6H_4\cdot CH_2\cdot CHO$, or colour bases, $NAr{:}CH\cdot C_6H_4\cdot CH{:}CH\cdot NHAr$, analogous to those obtained in the pyridine series (A., 1904, i, 448, 921; 1905, i, 467, 923; 1907, i, 625).

2-op-*Dinitrophenylisoquinolinium chloride*,

$$C_6H_3(NO_2)_2\cdot NCl{<}{{}^{CH\cdot C_6H_4}_{CH:CH}},$$
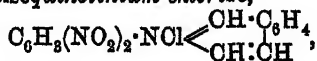
decomp. 130°, stout, rhombic crystals, is obtained by keeping an ethereal solution of *iso*quinoline and 1-chloro-2 : 4-dinitrobenzene for

several weeks or months at the ordinary temperature. It forms a *platinichloride*, m. p. 222°, and *periodide*, $C_{15}H_{10}O_4N_3I_8$, dark brown needles, and is readily hydrolysed by hot aqueous sodium nitrite, yielding *iso*quinoline, hydrogen chloride, and 2 : 4-dinitrophenol (in the form of the dinitrophenyl*iso*quinolinium and *iso*quinoline salts; the latter has m. p. 127°). Hydrogen sulphide decomposes the chloride, 2 : 4-dinitrophenyl mercaptan being produced in the aqueous solution and 2 : 4-dinitrophenyl sulphide in alcoholic solution.

Dinitrophenyl*iso*quinolinium chloride is converted by aqueous ammonia or sodium carbonate or by an aqueous solution of methyl-amine or aniline, less satisfactorily by aqueous sodium hydroxide, into the ψ *base*, $C_6H_8(NO_2)_2 \cdot N {<}^{CH(OH) \cdot C_6H_4}_{CH =\!=\!= CH}$, orange-red needles, m. p. 141—142°, darkening at about 90°, which is reconverted into dinitrophenyl*iso*quinolinium chloride by dilute hydrochloric acid, and yields ethers, $C_6H_8(NO_2)_2 \cdot N {<}^{CH(OR) \cdot C_6H_4}_{CH =\!=\!= CH}$, by warming with alcohols; the *methyl ether*, m. p. 149°, dark red crystals, *ethyl ether*, m. p. 135°, pale red prisms, and iso*butyl ether*, m. p. 122°, orange-red crystals, have been prepared. These ethers, which are also produced directly from dinitrophenyl*iso*quinolinium chloride and ammonia dissolved in the alcohol, are converted one into another by warming with the necessary alcohol.

By heating with water at 90—95° for some hours, or with acetone at 100°, or with boiling acetic anhydride, the freshly precipitated ψ-base is converted into an *isomeride*, m. p. 151°, dark red crystals with a violet shimmer. The isomeride is only slowly attacked by warm dilute hydrochloric acid, does not form ethers by boiling with alcohols, and is slowly converted into dinitrophenyl*iso*quinolinium chloride by hot concentrated hydrochloric acid. It does not react with phenylhydrazine, and is, therefore, not the aldehydo-base, $CHO \cdot C_6H_4 \cdot CH{:}CH \cdot NH \cdot C_6H_8(NO_2)_2$; probably it has the constitution $NHR \cdot CH{:}CH \cdot C_6H_4 \cdot CH(OH) \cdot O \cdot CH {<}^{NR - CH}_{C_6H_4 \cdot CH}$ [where R is $C_6H_8(NO_2)_2$], and is formed by the union of the ψ-base and the aldehydo-base.

When boiled in alcoholic solution with aniline or *p*-toluidine, dinitrophenyl*iso*quinolinium chloride or, better, the ψ-base or the violet isomeride is decomposed into 2:4-dinitroaniline and the 2-aryl*iso*quinolinium chloride. 2-*Phenyliso*quinolinium chloride, $C_{15}H_{12}NCl, 2H_2O$, long needles, forms a *platinichloride*, m. p. 228—229°, orange needles, and *mercurichloride*, m. p. 183—184°; the *dichromate*, decomp. about 195°, and *picrate*, m. p. 136—137°, yellow needles, are described. 2-*p*-*Tolyl*iso-*quinolinium chloride*, $C_{16}H_{14}NCl, 2H_2O$, colourless needles, forms a *platinichloride*, m. p. 216—217°, orange-yellow needles.

Dinitrophenyl*iso*quinolinium chloride is converted into the ψ-base by hydrazine hydrate, but reacts with phenylhydrazine in boiling alcohol just as does dinitrophenylpyridinium chloride (A., 1904, i, 448), yielding the *dinitroanilinophenylhydrazone*,

$$C_6H_8(NO_2)_2 \cdot NH \cdot CH{:}CH \cdot C_6H_4 \cdot CH{:}N \cdot NHPh,$$
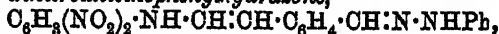
m. p. 183—184°, black needles. In a similar manner the *dinitro-anilino*-p-*tolylhydrazone*, $C_{22}H_{19}O_4N_5$, m. p. 185—186°, black leaflets with a red shimmer, and the *dinitroanilino-phenylmethylhydrazone*, $C_{22}H_{19}O_4N_5$, m. p. 181—182°, reddish-brown leaflets, have been obtained. These three substances are decomposed by boiling alcohol and hydrochloric acid, D 1·19, into 2 : 4-dinitroaniline and 2-*anilino*iso-quinolinium chloride, $C_9H_7N(NHPh)Cl$, m. p. 198—200°, faintly yellow, monoclinic prisms (*platinichloride*, m. p. 190° [decomp.]), 2-p-*toluidino*isoquinolinium *chloride*, rhombic plates, and 2-*methylanilino*-isoquinolinium *chloride*, faintly yellow needles (*picrate*, m. p. 170°; *platinichloride*, m. p. 185°; *mercurichloride*, m. p. 174°), respectively. 2-Anilino*iso*quinolinium chloride yields *iso*quinoline (aniline could not be detected) by reduction with zinc dust and dilute hydrochloric acid, and by treatment with aqueous sodium hydroxide, sodium carbonate, or ammonia yields a red precipitate which is apparently a mixture of the

ψ-base, $C_9H_4{<}^{CH(OH)\cdot N\cdot NHPh}_{CH=\!=\!=CH}$, and the azo-compound,

$C_6H_4{<}^{CH:N:NPh}_{CH:CH}$. C. S.

Bromination of 6-Methylquinoline and 6-Quinolinealdehyde.

JOHANN HOWITZ and J. PHILIPP (*Annalen*, 1913, **396**, 23—37).—The dibromide of 6-methylquinoline hydrobromide is obtained as a brick-red, crystalline powder by saturating a cold chloroform solution of 6-methylquinoline with hydrogen bromide and subsequently adding bromine (1 mol.). By carefully heating it at 170—180° for two hours, cooling to 140°, and adding more bromine (1 mol.), and heating again at 170—180° for two hours, the substance is converted into 6-*dibromomethylquinoline*, $C_9NH_6\cdot CHBr_2$, m. p. 159—160°, white needles (*platinichloride*, $2C_{10}H_7NBr_2,H_2PtCl_6$, m. p. 235°, orange crystals), and 3-*bromo* 6-*dibromomethylquinoline*, $C_{10}H_6NBr_3$, m. p. 141°, yellowish-white needles, each of which loses two atoms of bromine by hydrolysis with alcoholic potassium hydroxide.

By boiling with water for ten to fifteen minutes and basifying, 6-dibromo-methylquinoline is converted into 6-*quinolinealdehyde*, $C_{10}H_7ON$, glistening needles containing H_2O, m. p. 55° (anhydrous, 75—76°), which exhibits the usual reducing and additive properties of an aldehyde. It yields quinoline 6-carboxylic acid by oxidation, forms a *platinichloride*, $2C_{10}H_7ON,H_2PtCl_6$, m. p. 244°, reddish-yellow needles, *aldazine*, $N_2(:CH\cdot C_9NH_6)_2$, m. p. 261°, yellow needles, *semicarbazone*, m. p. 239°, *oxime*, m. p. 191°, *phenylhydrazone*, m. p. 185°, yellow crystals containing H_2O, *anil*, $NPh:CH\cdot C_9NH_6$, m. p. 99°, and o-*tolil*, m. p. 97°, and condenses with dimethylaniline in the presence of zinc chloride to form *tetramethyldiaminodiphenyl-6-quinolylmethane*,

$C_9NH_6\cdot CH(C_6H_4\cdot NMe_2)_2$,
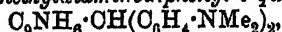
m. p. 160°, almost colourless needles, which yields a green *dye* by oxidation with lead peroxide. When heated with methyl iodide at 100°, 8-quinolinealdehyde yields a *methiodide*, $CHO\cdot C_9H_6NMeI$, m. p. 218°; the latter is oxidised by cold alkaline potassium ferricyanide to

1-*methyl*-2-*quinolone*-6-*aldehyde*, $CHO\cdot C_9H_5{<}^{NMe\cdot CO}_{CH=CH}$, m. p. 164°,

colourless needles, or the corresponding *acid*, $C_{11}H_9O_3N$, m. p. above 300°, according to the duration of the reaction.

3-Bromo-6-dibromomethylquinoline is hydrolysed by an excess of potassium carbonate and a little water at 115—120°, yielding *3-bromo-quinoline-6-aldehyde*, m. p. 139°, white needles (*aldazine*, m. p. 194°, pale yellow needles, *oxime*, m. p. 217°; *phenylhydrazone*, m. p. 195°; *anil*, m. p. 124°), in which the position of the halogen is determined by its oxidation to 3-bromopyridine-5 : 6-dicarboxylic acid by hot alkaline potassium permanganate. By oxidation with chromic and sulphuric acids, the aldehyde yields *3-bromoquinoline-6-carboxylic acid*, m. p. 245°, long white needles.   C. S.

8-Quinolyl Ketones and their Derivatives. JOHANN HOWITZ and O. KOPKE (*Annalen*, 1913, **396**, 38—52).

—Hitherto, only quinolyl ketones have been known containing the carbonyl group attached to the pyridine nucleus. Bromoquinolines and 8-bromomethylquinoline do not react with magnesium in ether. The interaction of 8-quinol-inealdehyde (Howitz and Schwenk, A., 1905, i, 471) and magnesium phenyl bromide in ether at 0°, leads to the formation of *phenyl-8-quinolylcarbinol*, $OH\cdot CHPh\cdot C_9NH_6$, m. p. 104°, large colourless plates, in about 60% yield. The carbinol forms a *platinichloride*, m. p. 198° (decomp.), and a *benzoate*, m. p. 146°, and is oxidised by chromic and acetic acids on the water-bath to *phenyl 8-quinolyl ketone*,

$$COPh\cdot C_9NH_6,$$
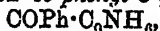
m. p. 94°, colourless plates (*platinichloride*, m. p. 213° [decomp.]). By treatment with hydroxylamine hydrochloride and potassium hydroxide in boiling alcohol, the ketone yields an *oxime*, $C_{16}H_{12}ON_2,H_2O$, m. p. 121°, which is converted into an *isomeride*, $C_{16}H_{12}ON_2,H_2O$, m. p. 165°, by heating at 120°, and then crystallising from alcohol. By treating a cold ethereal solution of the oxime, m. p. 121°, with phosphorus pentachloride, and decomposing the precipitated imino-chloride with water at 0°, *8-benzoylaminoquinoline*, $C_9NH_6\cdot NHBz$, m. p. 93°, is obtained, the identity of which is established by its formation by the benzoylation of 8-aminoquinoline and by its decomposition into 8-aminoquinoline and benzoic acid by concentrated hydrochloric acid at 160°. The oxime, m. p. 121°, is therefore anti-*phenyl 8-quinolyl ketoxime*, $\begin{matrix} C_9NH_6\cdot CPh \\ HO\cdot N \end{matrix}$. In a similar manner, the oxime, m. p. 165°, is proved to be syn-*phenyl 8-quinolyl ketoxime*, $\begin{matrix} C_9NH_6\cdot CPh \\ N\cdot OH \end{matrix}$, by its conversion by the Beckmann transformation into the anilide of quinoline-8-carboxylic acid; unfortunately, neither the anilide nor the quinolinecarboxylic acid produced by its hydrolysis has been isolated, but only the aniline resulting in the latter operation.

Phenyl 8-quinolyl ketone forms a *phenylhydrazone*, m. p. 190°, *semicarbazone*, m. p. 188°, and *azine*, $C_{32}H_{22}N_4$, m. p. 287°.

8-Quinolylmethylcarbinol, $OH\cdot CHMe\cdot C_9NH_6$, m. p. 65° (*platini-chloride*, m. p. 197° [decomp.], orange-yellow crystals; *benzoate*, m. p. 100°), obtained ultimately from magnesium methyl iodide and 8-quinolinealdehyde in ether, is oxidised to *8-quinolyl methyl ketone*, $C_9NH_6\cdot COMe$, m. p. 45°, b. p. about 295°, by potassium dichromate

and very dilute sulphuric acid on the water-bath. The ketone forms a *semicarbazone*, m. p. 223°, and an *oxime*, m. p. 137°; the latter has only been obtained in one modification, which is *syn*-8-quinolyl methyl ketoxime, since it yields 8-acetylaminoquinoline by the Beckmann transformation.

8-*Quinolylethylcarbinol* (*platinichloride*, m. p. 210° [decomp.]; *benzoate*, m. p. 82°) and 8-*quinolyl ethyl ketone*, b. p. about 290° (*semicarbazone*, m. p. 203°), have been prepared by methods similar to the preceding.

C. S.

Preparation of 9-Methylcarbazole. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 255304).—The technically valuable 9-methylcarbazole can be prepared in about 70% yield by the following method.

Dry potassium carbazole is heated with freshly distilled ethyl chloroacetate during about three hours, yielding *ethyl carbazole-9-acetate*, m. p. 97°; this when hydrolysed with an alkaline hydroxide gives rise to *carbazole-9-acetic acid*, glistening, colourless leaflets, m. p. 215°, which, when carefully heated at 250—270°, evolves carbon dioxide and furnishes pure 9-methylcarbazole, m. p. 87°. F. M. G. M.

Kehrmann's Interpretation of Chromo-Isomeric Acridonium Salts as "Quinhydrone Salts" which Contain Hydroacridine. ARTHUR HANTZSCH (*Ber.*, 1913, 46, 682—684. Compare this vol., i, 298).—Kehrmann's view that the dark green iodide obtained from methylphenazonium salts is a quinhydrone salt composed of one molecule of azonium tri-iodide and two molecules of methyldihydrophenazine, is combated.

According to Kehrmann, the salt should be decomposed by water into phenylmethylacridonium iodide, phenylmethylhydroacridine, and hydrogen iodide, but in reality it gives a clear, neutral solution, and behaves as a normal binary electrolyte. J. C. W.

"Halochromism" of the Derivatives of Phenyl*iso*oxazolone and of the Indogenides. ANDRÉ MEYER (*Compt. rend.*, 1913, 156, 714—717. Compare Baeyer and Villiger, A., 1901, i, 658; 1902, i, 380, 769; Meyer, A., 1912, i, 1019).—The indogenides and in particular the *iso*oxazole-indogenides give coloured compounds with acids and metallic salts, comparable to the oxonium salts, and the author has prepared a number of such compounds.

On passing dry hydrogen chloride into a suspension of piperonylidene-*iso*oxazolone in benzene at − 10°, a deep red additive *compound* is formed and crystallises out.

Condensation products are also formed from the *iso*oxazolones and stannic chloride, ferric chloride, or aluminium chloride, and a number of such stannichlorides, prepared by the addition of anhydrous staunic chloride to benzene solutions of the *iso*oxazolones, are described.

Phenylbenzylideneisooxazolone stannichloride, $C_{16}H_{11}O_2N,SnCl_4$, a yellow, microcrystalline powder, decomposes at 200°.

Phenylpiperonylidene-isooxazolone stannichloride, $C_{17}H_{11}O_4N,SnCl_4$, deep red leaflets, decomposes at 160°.

Phenylanisylideneisooxazolone stannichloride, $C_{17}H_{13}O_3N,SnCl_4$, a deep yellow powder, decomposes at 155°.

Phenyl-o-methoxybenzylideneisooxazolone stannichloride,
$$2C_{17}H_{13}O_3N,SnCl_4,$$
an orange powder, decomposes at 130°.

Phenylvanillylideneisooxazolone stannichloride, $C_{17}H_{13}O_4N,SnCl_4$, a brownish-red, microcrystalline powder, decomposes at 150°.

Phenyldimethylaminobenzylideneisooxazolone stannichloride,
$$C_{18}H_{16}O_2N_2,2SnCl_4,$$
a bright red powder, decomposes above 250°.
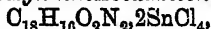
The indogenides furnish similar compounds, such as *piperonylidene-hydroxythionaphthen stannichloride*, $C_{15}H_{10}O_3S,SnCl_4$, a violet-black, microcrystalline powder, decomposing at 230°.

All these substances are hydrolysed by water and are practically insoluble in organic solvents, their colours being deeper than those of the parent substances.

The mixed azo-derivatives of phenylisooxazolone are also "halo-chromes" and give coloured stannichlorides, the one described being *benzeneazophenylisooxazolone stannichloride*, $C_{15}H_{11}O_2N_3,SnCl_4$, an orange-yellow powder, decomposing at 130°.   W. G.

Some Derivatives of the Methoxyphenylisooxazolones. ANDRÉ WAHL and C. SILBERZWEIG (*Bull. Soc. chim.*, 1913, [iv], 13, 236—240. Compare Wahl and Meyer, A., 1908, i, 368; Wahl, *ibid.*, 1909, i, 260).—The authors have condensed *o*-, *m*-, and *p*-methoxyphenyl-*isooxazolone* with a number of aldehydes, and have thus prepared the following substances : 3-o-*methoxyphenyl-4-benzylideneisooxazolone*, yellow leaflets, m. p. 150°; 3-m-*methoxyphenyl-4-benzylideneisooxazolone*, yellow needles, m. p. 110°; 3-p-*methoxyphenyl-4-benzylideneisooxazolone*, yellow leaflets, m. p. 170°; 3-o-*methoxyphenyl-4-anisylideneisooxazolone*, pale yellow, m. p. 154°; 3-m-*methoxyphenyl-4-anisylideneisooxazolone*, yellow crystals, m. p. 164°; 3-p-*methoxyphenyl-4-anisylideneisooxazolone*, pale yellow leaflets, m. p. 165°; 3-o-*methoxyphenyl-4-cinnamylideneiso-oxazolone*, orange-yellow, m. p. 163°; 3-m-*methoxyphenyl-4-cinnamyli-deneisooxazolone*, orange-yellow, m. p. 146—147°; 3-p-*methoxyphenyl-4 cinnamylideneisooxazolone*, orange needles, m. p. 163°; 3-o-*methoxy-phenyl-4-furfurylideneisooxazolone*, yellow crystals, m. p. 171—172°; 3-p-*methoxyphenyl-4-furfurylideneisooxazolone*, yellow needles, m. p. 141—142°; 3-o-*methoxyphenyl-4-p-dimethylaminobenzylideneisooxazolone*, red needles, m. p. 190°; 3-m-*methoxyphenyl-4-p-dimethylaminobenzyli-deneisooxazolene*, red needles, m. p. 140°; 3-p-*methoxyphenyl-4-p-di-methylaminobenzylideneisooxazolone*, red leaflets, m. p. 192°; 3-p-*methoxy-phenyl-4-o-hydroxybenzylideneisooxazolone*, yellow leaflets, m. p. 195°; 3-o-*methoxyphenyl-4-p-hydroxybenzylideneisooxazolone*, orange-yellow, m. p. 218°; 3-m-*methoxyphenyl-4-p-hydroxybenzylideneisooxazolone*, yellow leaflets, m. p. 215°; 3-p-*methoxyphenyl-4-p-hydroxybenzylideneisooxazolone*, golden-yellow needles, m. p. 204—205°; 3-o-*methoxyphenyl-4 p-hydroxy-m-methoxybenzylideneisooxazolone*, yellow crystals, m. p. 168°; 3-m-*methoxyphenyl-4-p-hydroxy-m-methoxybenzylideneisooxazolone*, orange-yellow crystals, m. p. 203°; 3-p-*methoxyphenyl-4-p-hydroxy-m-methoxy-benzylideneisooxazolone*, yellow crystals, m. p. 199°; 3-o-*methoxyphenyl-*

4-mp-*dihydroxybenzylidene*isooxazolone, orange crystals, m. p. 209°;
3-m-*methoxyphenyl*-4-mp-*dihydroxybenzylidene*isooxazolone, orange-red
needles, m. p. 184°; 3-p-*methoxyphenyl*-4-mp-*dihydroxybenzylidene*iso-
oxazolone, orange crystals, m. p. 193°; with o-vanillin, the 3-o- and
p-methoxyphenyl*isooxazolones* form yellow *leaflets*, m. p. 195°, and
orange-yellow *leaflets*, m. p. 208°, respectively, whilst with resorcyl
aldehyde, 3-o-, m- and p-methoxyphenyl*isooxazolones* yield orange-
yellow *crystals*, m. p. 235°, orange-yellow *crystals*, m. p. 240°, and
yellow *crystals*, m. p. 209°, respectively. The phenolic derivatives
dissolve in alkali, forming solutions in which the colour varies from
yellow to reddish-violet. Presence of excess of alkali rapidly discharges
these colorations, yielding colourless solutions from which acids
re-precipitate the original substance. The action of excess of alkali
probably causes a rupture of the lactonic grouping according to the
scheme:

$$O<\begin{matrix}CO\cdot C\colon CH\cdot R\\ N=C\cdot C_6H_4\cdot OCH_3\end{matrix} \quad \underset{HCl}{\overset{NaOH}{\rightleftarrows}} \quad \begin{matrix}CO_2Na\cdot C\colon CH\cdot R\\ HO\cdot N=C\cdot C_6H_4\cdot OCH_3\end{matrix}\cdot$$

The three methoxyphenyl*isooxazolones* have been condensed with
5-bromoisatin chloride, yielding the three 3-*methoxyphenyl*isooxazolone-
5-*bromo-2-indoles*,

$$\begin{matrix}N\colon C\cdot C_6H_4\cdot OCH_3\\ O\underline{\quad\quad} CO\end{matrix}>C\colon C<\begin{matrix}NH\\ CO\end{matrix}>C_6H_3Br,$$ the proper-

ties of which are similar to those of the previously described indigoid
dyes derived from the three methoxyphenyl*isooxazolones* and isatin
chloride. If, however, sodium hyposulphite is added to their solution
in alkali, the yellow colour of the latter persists. Addition of acid
causes the formation of a flocculent, yellow *precipitate*. The latter
dissolves in alcohol, forming a red solution, the colour of which deepens
on addition of an oxidising agent, the initial dye being ultimately
formed. The yellow precipitate appears to be the leuco-derivative
of the dye. It presents no marked affinity for the textile fibres.

H. W.

**Action of Acetic Anhydride on some Benzylideneanthranilic
Acids. II.** John B. Ekeley and Stiles Clinton (*J. Amer. Chem.
Soc.*, 1913, **35**, 282—284).—Ekeley and Dean (A., 1912, i, 211) have
shown that a series of oxazines can be obtained by the action of acetic
anhydride on benzylideneanthranilic acids. The reaction seems to be
of general application, and further compounds are now described.

Protocatechuylideneanthranilic acid, m. p. 204°, obtained by the
condensation of protocatechualdehyde with anthranilic acid, forms
orange-red crystals, and is converted by acetic anhydride into 4-*acetyl*-
3-(3′ : 4′)*dihydroxyphenyldihydro*-2 : 4-*benzoxazine*-1-*one*,

$$C_6H_4<\begin{matrix}CO\underline{\quad}O\\ NAc\cdot CH\cdot C_6H_3(OH)_2\end{matrix},$$
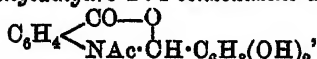
m. p. 121°. *Bromosalicylideneanthranilic acid*, m. p. 198°, crystallises in
yellow needles, and furnishes 4-*acetyl*-3-(4′ : 2′-)*bromohydroxyphenyldi-
hydro*-2.4-*benzoxazine*-1-*one*, m. p. 170°. o-*Nitrobenzylideneanthranilic
acid*, m. p. 67°, forms straw-coloured needles, and yields 4-*acetyl*-3-o-
nitrophenyldihydro-2:4-*benzoxazine*-1-*one*, m. p. 167·5°. o-*Methoxybenzyl-
ideneanthranilic acid*, m. p. 122°, gives 4-*acetyl*-3-o-*methoxyphenyldihydro*-
2:4-*benzoxazine*-1-*one*, m. p. 165°. *Resorcylideneanthranilic acid* begins to

decompose at about 150°; *4-acetyl-3-(1:3)-dihydroxyphenyldihydro-2:4-benzoxazine-1-one* has m. p. 192°. p-*Dimethylaminobenzylidene-anthranilic acid*, m. p. 176°, yields *4-acetyl-3-p-dimethylaminophenyl-dihydro-2:4-benzoxazine-1-one*, m. p. 162°.　　　　　　　　　E. G

A Gelatinous Mercury Salt of an Organic Sulphonic Acid.
W. DOHLE and BERTHOLD RASSOW (*Zeitsch. Chem Ind. Kolloide*, 1913, 12, 71—74).—By the action of fuming sulphuric acid on benzothiazole-methenesulphide, a monosulphonic acid of the composition :

$$C_8H_6NS_2 \cdot SO_3H$$
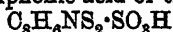
is obtained. When aqueous solutions of the potassium salt and of mercuric chloride are mixed together, a yellow solution is obtained, which, sooner or later, depending on the concentration, solidifies to a jelly. The jelly-forming substance is the normal mercuric salt, and its activity is such, that even in $N/100$-solution it is capable of producing a jelly at the ordinary temperature. The mercury salt is unstable, and the jellies sooner or later become cloudy in consequence of the formation of the basic salt, $Hg(C_8H_6NS_2 \cdot SO_3)_2, HgO$, which separates out in the form of very small crystals. The stability of the jellies increases with the concentration of the mercury salt and those prepared from $N/5$-solutions of the potassium salt and mercuric chloride can be kept for some time before they begin to exhibit opalescence as a result of the initial precipitation of the basic salt.

The colloidal mercury salt is coagulated by electrolytes and alcohol, the coagulum being converted into the crystalline basic salt on contact with water.

From the examination of freshly prepared solutions of the mercury salt, it has been found that the viscosity increases with time, the rate of increase varying very considerably from one solution to another even when the conditions under which the solutions were prepared, were exactly the same. Most electrolytes increase the viscosity, but potassium iodide increases it to a remarkable extent.　　　　H. M. D.

Aromatic ψ-Thiocarbamides and Orthothiocarbonic Esters.
FRITZ ARNDT (*Annalen*, 1913, 396, 1—22. Compare A., 1911, i, 918).—*Phenyl-ψ-thiocarbamide*, $NH:C(NH_2) \cdot SPh$, m. p. 96—97° (decomp.), glistening needles, prepared from phenyl mercaptan and cyanamide, forms a sparingly soluble *nitrate-sulphate*,

$$3C_7H_8N_2S, H_2SO_4, HNO_3,$$
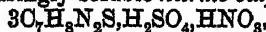
m. p. 206° (decomp.), which, however, is distinctly more soluble than the nitrate-sulphate of p-tolyl-ψ-thiocarbamide (*loc. cit.*) ; in fact, the salts of phenyl-ψ-thiocarbamide are much more soluble than those of the p-tolyl homologue. p-*Chlorophenyl-ψ-thiocarbamide*,

$$NH:C(NH_2) \cdot S \cdot C_6H_4Cl,$$
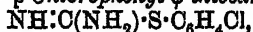
forms a *nitrate-sulphate*, $3C_7H_7N_2SCl, H_2SO_4, HNO_3$, m. p. 222° (decomp.).

The substance previously described as nitroso-p-tolyl-ψ-thiocarbamide (*loc. cit.*) is now shown to be the p-tolyl-ψ-carbamide salt of *dinitroso* p-*tolyl-ψ-thiocarbamide*, $OH \cdot N:N \cdot O(SC_7H_7):N \cdot NO$. The salt is decomposed by cold glacial acetic acid into nitrogen and p-tolyl thiocyanate, and by cold concentrated hydrochloric acid into nitrous acid and p-tolyl-ψ-thiocarbamide. The yellow substance obtained by

its decomposition by boiling methyl alcohol receives the constitution $C_7H_7S\cdot CO\cdot N\!:\!NOH$, since it yields p-tolylthiocyanate and mercaptan by treatment with concentrated hydrochloric acid. By gradually adding the p-tolyl-ψ-thiocarbamide salt of dinitroso-p-tolyl-ψ-thiocarbamide to a gently boiling methyl-alcoholic solution of potassium acetate (saturated in the cold), the *potassium* salt,

$$C_8H_7O_2N_4SK,H_2O,$$
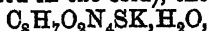
of the dinitroso-derivative is obtained. It crystallises in glistening needles, yields the *calcium*, *barium*, and *ferric* salts by double decomposition, and the *benzamidine* salt, white leaflets, by treatment with aqueous benzamidine hydrochloride, and by the action of dilute acetic acid yields the free dinitroso-compound, which, however, instantly decomposes into nitrous acid and *nitroso-p-tolyl-ψ-thiocarbamide*,

$$C_7H_7S\cdot C(\!:\!NH)\cdot N\!:\!N\cdot OH,$$

decomp. 115—120°, golden-yellow leaflets. The latter yields nitrous acid and p-tolyl-ψ-thiocarbamide by treatment with concentrated hydrochloric acid, and nitrogen and p-tolyl thiocyanate with warm glacial acetic acid. By treatment with sodium nitrite and hydrochloric acid, phenyl-ψ-thiocarbamide and p-chlorophenyl-ψ-thiocarbamide each yield ψ-thiocarbamide salts of the dinitroso-ψ-thiocarbamide.

As mentioned previously (*loc. cit.*), p-tolyl *ortho*-thiocarbonate is obtained by treating a methyl-alcoholic solution of the p-tolyl-ψ-thiocarbamide salt of dinitroso-p-tolyl-ψ-thiocarbamide with aqueous ammonia. This reaction could not be explained when the p-tolyl-ψ-thiocarbamide salt was considered to be a nitroso-compound. Its course is now clear. The ammonia liberates p-tolyl-ψ-thiocarbamide and converts it into p-tolyl mercaptan, which then reacts with the dinitroso-compound (or its ammonium salt) in accordance with the equation: $C_7H_7S\cdot C(\!:\!N\cdot NO)\cdot N\!:\!N\cdot OH + 3C_7H_7\cdot SH = C(SC_7H_7)_4 + 2N_2 + 2H_2O$. The orthothiocarbonate is also obtained by treating a methyl-alcoholic solution of the p-tolyl-ψ-thiocarbamide salt or the potassium salt of dinitroso-p-tolyl-ψ-thiocarbamide directly with p-tolyl mercaptan.

Phenyl orthothiocarbonate, $C(SPh)_4$, m. p. 159°, small leaflets, and p-*chlorophenyl orthothiocarbonate*, $C(S\cdot C_6H_4Cl)_4$, m. p. 212—213°, are prepared by methods similar to the preceding. p-*Chlorophenyl orthothioformate*, $CH(S\cdot C_6H_4Cl)_3$, m. p. 111—112°, almost colourless leaflets, is obtained by boiling p-chlorophenyl mercaptan in aqueous sodium hydroxide with an excess of chloroform. *Phenyl tri-p-chlorophenyl orthothiocarbonate*, $SPh\cdot C(S\cdot C_6H_4Cl)_3$, small, white leaflets, m. p. about 191°, obtained by warming potassium dinitrosophenyl-ψ-thiocarbamide and the calculated amount of p-chlorophenyl mercaptan in methyl alcohol, is converted by crystallisation from acetic acid into a mixture of the tetraphenyl and the tetra-p-chlorophenyl esters of orthothiocarbonic acid; the latter has been isolated. *Tri-p-chlorophenyl-p-tolyl orthothiocarbonate*, m. p. about 193°, is prepared in a similar manner, and also tends to change to the unmixed esters. By reduction with boiling glacial acetic acid and zinc dust, it is converted into *di-p-chlorophenyl-p-tolyl orthothioformate*, $C_7H_7S\cdot CH(S\cdot C_6H_4Cl)_2$, m. p. 96—97°, white leaflets, which is not changed by crystallisation from glacial acetic acid.   C. S.

Preparation of 6-Aminodiarylamino- and 7-Aminodiaryl-amino-1-naphthol-3-sulphonic Acids with their Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254510).— Numerous compounds obtained by the condensation of aromatic benzenoid amines with aminonaphthols in the presence of sodium hydrogen sulphite have been previously described (A., 1905, i, 585), and the reaction has now been extended to the diphenyl series.
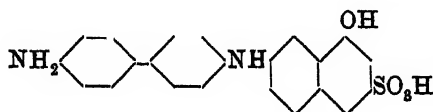
4'-*Amino*-7-*diphenylamino*-1-*naphthol*-3-*sulphonic acid* (annexed formula) is obtained when 1 : 7-dihydroxynaphthalene-3-sulphonic acid (240 parts) is boiled during forty-eight hours with benzidine (184 parts) and an aqueous solution of sodium hydrogen sulphite (2400 parts); the *sodium* salt forms grey leaflets.

The following compounds are also described : 3'-*sulpho*-4'-*amino*-6-*diphenylamino*-1-*naphthol*-3-*sulphonic acid* ; 3'-*sulpho*-4'-*amino*-7-*diphenylamino*-1-*naphthol*-3-*sulphonic acid*, from 7-amino-1-naphthol-3-sulphonic acid with benzidinesulphonic acid ; 4'-*amino*-6-*diphenyl-amino*-1-*naphthol*-3-*sulphonic acid*, from benzidine with 1 : 7-dihydroxy-naphthalene-3-sulphonic acid ; and the *compound*, from 7-amino-1-naphthol-3-sulphonic acid with benzidinesulphonic acid and a mixture of ammonium and sodium hydrogen sulphites ; the *sodium* salt forms glistening, grey leaflets.   F. M. G. M.

Catalytic Decomposition of Phenylhydrazine by Cuprous Salts. ALEXANDER E. ARBUZOV and V. M. TICHVINSKI (*J. Russ. Phys. Chem Soc*, 1913, **45**, 69—70).—When heated with cuprous chloride, bromide or iodide, phenylhydrazine undergoes catalytic decomposition according to the equation :

$$3NHPh\cdot NH_2 + CuX = 3NH_2Ph + N_2 + NH_3 + CuX$$

(compare Struthers, P., 1905, 95). In all cases, an unstable intermediate compound is formed, that given by the iodide having the composition $CuI,2NHPh\cdot NH_2$. Cuprous chloride is the most effective and the iodide the least so.   T. H. P.

A Process for the Preparation of New Colouring Matters and its Application. BRONISLAW PAWLEWSKI (*Bull. Soc. ind. Mulhouse*, 1912, **82**, 682—683).—When aniline in acid or alcoholic solution is oxidised at 50—60° with ammonium persulphate, a black *dye* is obtained, which is considered to be bisimino-*p*-benzoquinone,

$$O{:}C_6H_4{:}N\cdot N{:}C_6H_4{:}O.$$
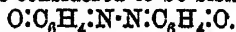
By changing the conditions, other brown or black anilinoquinones are formed. Similar colouring matters containing oxygen have been prepared from *m*-phenylenediamine, *o*-dianisidine, and benzylaniline. They are easily fixed by cotton, linen or silk, with or without the aid of mordants.   J. C. W.

Preparation of 1-*p*-Bromo-4-iodophenyl- and of 4-Bromo-1-*p*-iodophenyl-2 : 3 dimethyl-5-pyrazolone. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 254487).—The introduction of bromine and iodine into the molecule of 1-phenyl-2 : 3-dimethyl-5-pyrazolone confers on it a markedly increased therapeutic activity.

1-p-*Bromo-4-iodophenyl*-2 : 3-*dimethyl-5-pyrazolone* (annexed formula), colourless crystals, m. p. 163°, is obtained when a benzene solution of *p*-bromophenyl-2 : 3-dimethyl-5-pyrazolone (A., 1900, i, 695) is treated with finely powdered iodine and heated at 50—60° during two hours, whilst 4-*bromo*-1-p-*iodophenyl* 2 : 3-*dimethyl-5-pyrazolone*, pale yellow leaflets, m. p. 170°, is prepared by the bromination of 1-*p*-iodophenyl-2 : 3-dimethyl-5-pyrazolone (A., 1907, i, 84).   F. M. G. M.
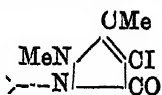
Hydantoins. XXI. Action of Ammonium and Potassium Thiocyanates on α-Amino-acids. TREAT B. JOHNSON and BEN H. NICOLET (*Amer. Chem. J.*, 1913, 49, 197—204).—In an earlier paper (this vol., i, 203), it has been pointed out that ammonium and potassium thiocyanates behave somewhat differently towards α-amino-acids. It has now been found that both salts combine with the acids to form the same thiohydantoins, but that the best yields are obtained by means of the ammonium salt.

When asparagine is treated with ammonium thiocyanate, 2-thio-3-acetylhydantoin-4-acetamide (Johnson and Guest, A., 1912, i, 807) is obtained in a yield amounting to 50% of the theoretical, whilst with the potassium salt a yield of only 6% is obtained.

Phenylalanine gives with ammonium thiocyanate a 94% yield of 2-thio-3-acetyl-4-benzylhydantoin, m. p. 170° (not 257° as stated by Johnson and O'Brien, A., 1912, i, 806); a somewhat smaller yield is obtained by the use of the potassium salt.

By the action of ammonium thiocyanate on tyrosine, a 94% yield is obtained of 2-*thio*-4-p-*hydroxybenzylhydantoin*,

$$\begin{array}{c}NH \cdot CO \\ CS \cdot NH\end{array}\!\!\!\!> OH \cdot CH_2 \cdot C_6H_4 \cdot OH,$$
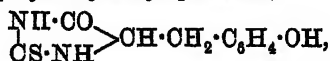
m. p. 211°, which forms pale yellow needles ; if potassium thiocyanate is employed, only a very small yield is obtained.

2-Thio-3-benzoylhydantoin (Johnson and Nicolet, A., 1912, i, 53) is obtained in 85—88% yield by the action of ammonium thiocyanate on hippuric acid, but in not more than 50% yield by the action of the potassium salt.

In the case of alanine, an excellent yield of 2-thiol-3-acetyl-4-methylhydantoin (Johnson, A., 1912, i, 390) is obtained with ammonium thiocyanate, but only about 34% with the potassium salt.

The thiohydantoin of pyrrolidonecarboxylic acid (Johnson and Guest, A., 1912, i, 317) is readily obtained in good yield by means of ammonium thiocyanate, but only in small amount by the action of the potassium salt.   E. G.

The Reactivity of the β-Unsubstituted Pyrrole Ring. III. Action of Cyanogen Bromide and Pyridine on Indoles. WALTER KÖNIG and R. SCHRECKENBACH (*J. pr. Chem.*, 1913, [ii], **87**, 241—257). —In view of the parallelism, previously shown to exist (A., 1911, i, 808), in the reactivity of primary aromatic amines and phenols on the one hand, and of 3-unsubstituted indole derivatives on the other, the author has examined the behaviour of the latter compounds toward pyridine and cyanogen bromide, and finds that they yield dyes which have the general formula :

$$NH{<}^{C_6H_4}_{OR}{>}C{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}C{<}^{C_6H_4}_{OR}{>}NHX,$$
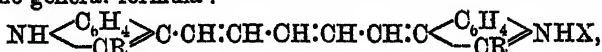
and are, therefore, closely related to the pyridine dyes derived from aromatic amines.

α-2-Methylindyl-ε-2-methylindolidene-Δαγ-pentadiene hydrobromide,

$$NH{<}^{C_6H_4}_{CMe}{>}C{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}C{<}^{C_6H_4}_{CMe}{>}NHBr,$$ is obtained in

lustrous, golden leaflets by the action of hot acetone on its additive *compound*, $C_{23}H_{21}N_2Br,C_5H_5N,HBr$, with pyridine hydrobromide. The latter compound separates in green needles by the successive addition of pyridine and cyanogen bromide in ethereal solution to 2-methylindole, dissolved in methyl alcohol. The *dihydrobromide*, prepared by warming the monohydrobromide with acetone and hydrobromic acid, crystallises in lustrous, silky, bluish-green needles.

On treatment with aqueous sodium hydroxide and methyl alcohol, the hydrobromide yields the *dye-base*, $C_{23}H_{20}N_2$. This forms bluish-black needles, and is converted at 220° into a yellow *substance*, m. p. 265°, which probably has the same composition as the original dye-base, yields a *phenylhydrazone* (decomp. 160—170°), and when heated at 160° under diminished pressure decomposes, yielding 2-methylindole. The dye-base reacts with phenylhydrazine in alcoholic solution, yielding 2-methylindole and the *phenylhydrazone*,

$$NH{<}^{C_6H_4}_{CMe}{>}C{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}N{\cdot}NHPh,$$
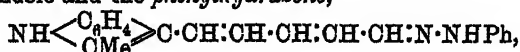
which forms an amorphous, light yellow powder (decomp. 170—180°) containing alcohol (1 mol.).

On treatment with dry hydrogen chloride, the dye-base yields a *hydrochloride*, $C_{23}H_{21}N_2Cl$; the *perchlorate*, $C_{23}H_{21}O_4N_2Cl$, forms small, compact, green crystals having a golden lustre, and crystallises with methyl alcohol in long, slender, bluish-green needles.

α-Indyl-ε-indolidene-Δαγ-pentadiene hydrobromide, $C_{21}H_{17}N_2Br$, prepared from indole, cyanogen bromide, and pyridine in methyl alcoholic solution, forms a microcrystalline, dark blue powder, containing pyridine (1 mol.).

α-2:4-Dimethylindyl-ε-2:4-dimethylindolidene-Δαγ-pentadiene hydrobromide, prepared from 2:4-dimethylindole, yields on treatment with aqueous sodium hydroxide and methyl alcohol the *dye-base*, $C_{25}H_{24}N_2$, which forms microcrystalline, bluish-black needles ; a *dihydrobromide* and a *perchlorate*, crystallising in green leaflets of a golden lustre, are also described.

The action of cyanogen bromide and pyridine on phloroglucinol and

resorcinol gives rise to blue pyridine dyes, which, however, are too unstable to be isolated. F. B.

[Preparation of 4-Chloro-5-bromoisatin.] KALLE & Co. (D.R.-P. 254468).—*4-Chloroisatin*, a yellow, crystalline powder, m. p. 254°, is prepared by treating a cooled acetic-chromic acid solution of 4 : 4'-dichloroindigotin with concentrated nitric acid ; when warmed with bromine (in acetic acid solution) it gives rise to *4-chloro-5-bromoisatin*, red needles, m. p. 255°, which on treatment with phosphorus pentachloride furnishes *4-chloro-5-bromoisatin chloride*, brown needles, m. p. 278° ; the corresponding anilide was also prepared.

F. M. G. M.

Preparation of 5 : 6 : 5' : 6'-Tetrachloroindigotin. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 254467).—*4 :5-Dichloro-2-nitrobenzaldehyde*, yellow prisms, m. p. 73°, is prepared by the nitration of 4 : 5-dichlorobenzaldehyde ; this when condensed with acetone in the presence of sodium hydrogen sulphite furnishes *dichloronitrophenyl-lactyl ketone*, m. p. 116°, which is readily converted by known methods into 5 : 6 : 5' : 6'-*tetrachloroindigotin*, a substance possessing valuable tinctorial properties. F. M. G. M.

Preparation of Dinitro-1 : 1'-dianthrimide. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 254186).—The nitration of dianthrimide (which has previously been described) takes place more smoothly and yields a definite characteristic product when carried out in the presence of boric acid.

1 : 1'-Dianthrimide (100 parts) and boric acid (65 parts) are dissolved in 1000 parts of concentrated sulphuric acid, treated at 5—10° with 27% nitric acid (122 parts), and left during two to three days at the ordinary temperature, when about 87% of the 4 : 4'-dinitro-1 : 1'-dianthrimide separates in glistening, coppery crystals. The m. p. is above 300°, and it is identical with the compound previously obtained by condensing 4-nitro-1-amino- with 4-chloro-1-amino-anthraquinone ; on reduction it furnishes 4 : 4'-diamino-1 : 1'-dianthrimide.

F. M. G. M.

Preparation of ω-Methylsulphites of Substituted Amino-arylpyrazolones. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 254711).—Compounds having valuable therapeutic properties are obtained when the substituted 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolones are heated with formaldehyde and sodium hydrogen sulphite ; *compounds* obtained in this manner from the following pyrazolones have now been prepared. From 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone, sintering and decomposing at 231—233° ; from 4-amino-1-*p*-tolyl-2 : 3-dimethyl-5-pyrazolone, sintering at 120°, decomposing at 125° ; from 1-*p*-aminophenyl-2 : 3-dimethyl-5-pyrazolone, isolated as its hygroscopic, crystalline *sodium* salt ; from 1-*p*-amino-phenyl-2 : 3 : 4-trimethyl-5-pyrazolone, also isolated as a crystalline

sodium salt; from 4-amino-1-*p*-ethoxyphenyl-2:3-dimethyl-5-pyrazolone, m. p. 113—115°, decomp. at 133—135°. The foregoing *4-amino-p-ethoxyphenyl-2 : 3-dimethyl-5-pyrazolone*, m. p. 132—133°, is obtained by the reduction of 4-nitroso-*p*-ethoxy-2 : 3-dimethyl-5-pyrazolone.

F. M. G. M.

Pyrimidines. LIX. Barbituryl- and 2-Thiobarbituryl-5-acetic Acids. TREAT B. JOHNSON and EDWARD F. KOHMANN (*Amer. Chem. J.*, 1913, **49**, 184—197).—An account is given of experiments undertaken with a view to the preparation of compounds containing condensed pyrimidine and pyrrole nuclei, and corresponding with the indoles and pyrindoles (Perkin and Robinson, T., 1912, **101**, 1787). Compounds of this new class are termed 1:6:8-, 1:5:7-, and 2:5:7-pyrimazoles (annexed formulæ).
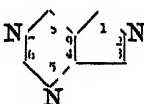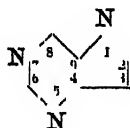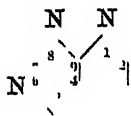
A 1:6:8-pyrimazole has already been obtained by heating ethyl 6-chloro-2-ethylthiolpyrimidine-5-acetate with alcoholic ammonia (A., 1911, i, 575); this compound, previously termed 2-ethylthiol-5:6-*a*-pyrrolidone-pyrimidine, is now designated 2-keto-7-ethylthiol-1:6:8-pyrimazole.

When ethyl ethane-*aaβ*-tricarboxylate is treated with carbamide in the presence of sodium ethoxide, the *sodium* salt of barbituryl-5-acetamide is obtained, which crystallises with $4H_2O$. *Barbituryl-5-acetamide*,

$$CO{<}^{NH \cdot CO}_{NH \cdot CO}{>}CH \cdot CH_2 \cdot CO \cdot NH_2,$$
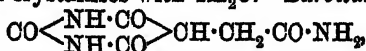
m. p. 258—261° (decomp.), crystallises in needles. *Barbituryl-5-acetic acid*, $CO{<}^{NH \cdot CO}_{NH \cdot CO}{>}CH \cdot CH_2 \cdot CO_2H$, obtained by the action of 20% hydrochloric acid on the sodium salt of the amide, separates in plates, becomes charred at 230°, and decomposes at 250°. An attempt to condense the amide to a 1:6:8-pyrimazole by the action of phosphoryl chloride on its sodium salt was not successful.

Thiobarbituryl-5-acetamide, $CS{<}^{NH \cdot CO}_{NH \cdot CO}{>}CH \cdot CH_2 \cdot CO \cdot NH_2, H_2O$,

prepared by the condensation of thiocarbamide with ethyl ethane-*aaβ*-tricarboxylate, crystallises in needles and decomposes at 272°; the *sodium* salt forms long, colourless prisms. *Thiobarbituryl-5-acetic acid*, $CS{<}^{NH \cdot CO}_{NH \cdot CO}{>}CH \cdot CH_2 \cdot CO_2H, 2H_2O$, crystallises in needles and decomposes above 230°.

Ethyl cyanosuccinate condenses with carbamide with formation of a pyrimidine. The reaction does not take place smoothly, and only small yields of condensation products are obtained. In one experiment, barbituryl 5-acetic acid was pro-

produced, together with 2 : 5 : 7-*triketo*-1 : 6 : 8-*pyrimazole* (formula I), which forms a brown powder and does not melt below 320°. In another experiment, barbituryl-5-acetic acid and 4-*iminobarbituryl-5-acetic acid*,
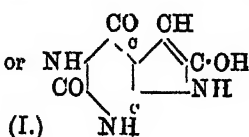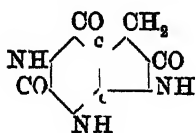
$$CO\underset{NH\cdot C(:NH)}{\overset{NH----CO}{<}}>CH\cdot CH_2\cdot CO_2H,$$
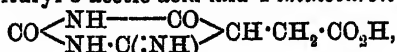
were isolated; the latter substance is a brown powder, and does not melt below 338°.   E. G.

Preparation of Azimino-[Triazole]-compounds in the Anthraquinone Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254745).—The azimino-compounds having the general formula $A<\underset{-N}{\overset{NR}{}}>N$, where A is anthraquinone and R hydrogen, alkyl or aryl groups, and prepared by the action of nitrous acid on *o*-diamino-anthraquinones, are of technical value for the preparation of dyes. The preparation of the following *compounds* is described: From 1 : 2-diaminoanthraquinone, needles; from 2 : 3-diaminoanthra-quinone, and from 1-*p*-tolylamino-2-amino-3-bromoanthraquinone, citron-yellow needles. The tinctorial properties of these compounds are enhanced by the introduction of halogens into the molecule.

F. M. G. M.

Polymeric Indoles. K. KELLER (*Ber.*, 1913, **46**, 726—733).— The high-boiling residue obtained in the distillation of practically pure indole consists of a trimeride, *tri-indole*, which after recrystalli-sation from benzene can be obtained in colourless crystals, m. p. 167°. The polymerisation can be better effected by heating indole with an aqueous solution of metaphosphoric acid. When distilled in a vacuum, tri-indole decomposes completely into indole; it gives a *monoacetyl* derivative, colourless crystals, m. p. 202°, and a *monobenzoyl* deriv-ative, colourless, crystalline powder, m. p. 207°. These acyl compounds are remarkably resistant to alkalis. When benzoyltri-indole is heated in a vacuum, indole distils away, leaving a residue of *benzoyldi-indole*, colourless needles, m. p. 198°; this resisted all attempts at acetylation and hydrolysis. The easiest method for the preparation of benzoyl-tri-indole is by boiling together a benzene solution of indole with anhydrous sodium carbonate and benzoyl chloride, whilst a slow current of hydrogen chloride is passed through the mixture; the yield is then 90% of the indole taken.

The action of hydrogen chloride on a solution of indole in benzene yields a colourless salt of composition

$$(C_8H_7N)_2,HCl,$$
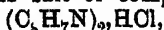
presumably *di-indole hydrochloride*, but it was not found possible to isolate the corresponding base in a pure state.

From a consideration of the behaviour of the above tri-indole derivatives, the annexed structure is suggested for the base, the reactive indole nucleus being that on the left; this differs from the remaining two by being attached to the rest of the molecule at carbon atoms which are each adjacent to nitrogen atoms. D. F. T.
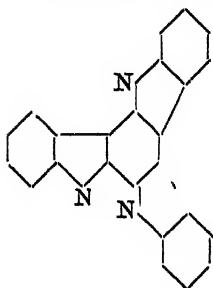
Preparation of Formaldehyde Derivatives of Xanthine and its Substitution Products. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254488).—When xanthine, its derivatives, or the purine bases are gently heated in aqueous or hydrochloric acid solution with formaldehyde (or its generators), they furnish *compounds* of marked therapeutic value. The following are described : (1) From 1 : 3-dimethylxanthine and formaldehyde in aqueous solution, contains 14% formaldehyde, m. p. 265° when slowly heated, but if suddenly subjected to a temperature of 165—170°, violent decomposition occurs with regeneration of 1 : 3-dimethylxanthine.

(2) From 3 : 7-dimethylxanthine with paraformaldehyde in fuming hydrochloric acid solution, it forms characteristic needles, contains 14% formaldehyde, and does not melt below 300°.

(3) From xanthine and formaldehyde, contains 32% formaldehyde ; and (4) from 3-methylxanthine contains 16% of formaldehyde. These compounds readily decompose in the organism with elimination of formaldehyde.   F. M. G. M.

The Anomalies in the Solubility of Uric Acid (Colloidal Uric Acid). HEINRICH SCHADE and E. BODEN (*Zeitsch. physiol. Chem.*, 1913, 83, 347—380).—If uric acid is suspended in boiling water, and alkali is then added very slowly until the mixture is just alkaline to phenolphthalein, the acid appears to pass into solution. This solution can be made by one of the following methods to set to a solid gel : (*a*) by the addition of concentrated sodium chloride solution ; (*b*) by addition of other salt solutions, such as ammonium sulphate, which are ordinarily employed for the precipitation of colloids ; (*c*) by addition of alcohol, and (*d*) by rapid cooling. The same phenomenon can be produced when the acid is neutralised by ammonia, lithium, sodium and potassium hydroxides, by the alkaline earths, and even ferric hydroxide. The appearance of the gel thus produced is described in great detail, and also the phenomena of its gradual transformation into the ordinary crystalline form. The colloid appears to be a supersaturated uric acid solution, in which the uric acid forms an adsorption compound with the alkali, which causes it to retain the colloidal form, and this adsorption compound appears to be a preliminary stage in the formation of the true chemical crystalline compound. The view here advanced can explain certain anomalies, to which Bechhold and Ziegler have called attention as regards the solubility of uric acid in serum.   S. B. S.

Purines. VIII. 2 : 8-Dihydroxy-1 : 9-dimethylpurine and 2-Hydroxy-6 : 9-dimethylpurine. CARL O. JOHNS (*J. Biol. Chem.*, 1913, 14, 1—7).—2 : 8-Dihydroxy-1 : 9-dimethylpurine is synthesised as follows : the potassium salt of 5-nitro-6-methylamino-2-hydroxypyrimidine (Johns, A., 1911, i, 506) when heated with methyliodide gives 5-*nitro-6-methylamino-2-hydroxy-3-methylpyrimidine*, the constitution of which is established by heating the methylated product with sulphuric acid, when 5-nitro-2 : 6-dihydroxy-3-methylpyrimidine (Behrend and Thurm, A., 1902, i, 833) is obtained.

On reducing the methylated product with freshly precipitated

ferrous hydroxide, it is converted into *5-amino 6-methylamino-2-oxy-3-methylpyrimidine*, $N<^{C(NHMe)\cdot C\cdot NH_2}_{CO\cdot NMe-CH}$. This is very soluble and purified only with difficulty. The crude base was accordingly heated with carbamide and converted into *2 : 8-dioxy-1 : 9-dimethylpurine*, $^{NMe\cdot CH:C\cdot NH}_{CO-N:C\cdot NMe}>CO$.

By heating the potassium salt of acetyl-5 : 6-diamino-2-oxy-4-methylpyrimidine, *2-oxy-6 : 9-dimethylpurine*,

$$^{N:CMe-C\cdot NH}_{CO\cdot NH\cdot C-N}>CMe,$$
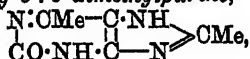
is obtained.

5-Nitro-6-methylamino-2-oxy-3-methylpyrimidine forms a bulky mass of hair-like crystals, m. p. 203°, to a colourless oil.

The *picrate* of *5-amino-6-methylamino-2-oxy-3-methylpyrimidine* crystallises in long prisms, m. p. 200° (decomp.).

2 : 8-Dioxy-1 : 9-dimethylpurine crystallises in small, irregular plates, which do not melt or char at 320°.

2-Oxy-6 : 8-dimethylpurine separates in small prisms with square ends, which slowly turn brown at 315°; they give a murexide reaction.
E. F. A.

Azomethines and Azo-dyes. CAMILLE G. VERNET (*Arch. Sci. phys. nat.*, 1913, [iv], 35, 148—172).—The azomethines derived from a number of diamines and benzaldehyde or its derivatives are described. In general they are formed quantitatively, the amount isolated depending on the manner in which the condensation is effected and the dilution of the solvents employed.

2-Mononitrobenzidine forms with benzaldehyde a yellowish-brown *compound*, m. p. 157°; with one molecule of *p*-nitrobenzaldehyde the product is red, m. p. 200—201°, with two molecules it is yellow, m. p. 205—206°; with dimethyl-*p*-aminobenzaldehyde it is yellow with an ill-defined melting point; with *o*-vanillin it is red, m. p. 200°·

m-Dinitrobenzidine and *o*-vanillin yield a reddish-brown product.

Benzidinesulphone combines with one molecule of benzaldehyde to a yellow compound, m. p. 259—260°; with *p*-nitrobenzaldehyde to a brown compound, m. p. 302—304°; with dimethyl-*p*-aminobenzaldehyde the compound is yellow, m. p. 318°; with *o*-vanillin it is yellowish-red.

Diaminodiphenylamine and benzaldehyde form a yellow compound, m. p. 184—185°; with *p*-nitrobenzaldehyde the compound is black with a metallic lustre, m. p. 219°; with dimethyl-*p*-aminobenzaldehyde it is very similar, m. p. 222°; with *o*-vanillin it is brick-red, m. p. 207—208°.

3 : 3'-Diaminocarbazole and benzaldehyde yield a yellow substance, m. p. 186°; the product with *p*-nitrobenzaldehyde is red, m. p. 306—307°; with dimethyl-*p*-aminobenzaldehyde it is yellowish-brown, m. p. 266—268°; with *o*-vanillin it is brick-red, m. p. 254—255°.

trans-o-Diaminostilbene and benzaldehyde form a yellow product, m. p. 188°; with *p*-nitrobenzaldehyde it is orange-red, m. p. 228°; with

dimethyl-*p*-aminobenzaldehyde it is yellow, m. p. 227°, and with *o*-vanillin it is red, m. p. 228°.

p-Diaminostilbene yields a yellow compound with benzaldehyde, m. p. 254°; an orange-red compound with *p*-nitrobenzaldehyde, m. p. 242°; a reddish-yellow product with dimethyl-*p*-aminobenzaldehyde, m. p. 233°, and a red product with *o*-vanillin.

These azomethines are all very similar; the nitro-group has a greater effect in intensifying the colour than the substituted amino-group.

Most of the compounds have a normal composition with both amino-groups condensed, but traces of the condensation products with a single molecule of aldehyde are formed at the same time.

A comparison is made of the colours obtained by soaking the material impregnated with sodium-β-naphthoxide in the diazotised solutions of a number of diamines   Whereas benzidine gives a brown, thiobenzidine and benzidinesulphone give reddish-brown shades, mononitrobenzidine gives a red, *m*-dinitrobenzidine an orange, and the *o*-dinitro-derivative a garnet-red. With 2 : 2'- or 3 : 3'-diamino-carbazole the colour is almost black, and *p*-diaminostilbene gives a similar colour. The replacement of an atom of hydrogen by a univalent grouping has more influence on the colour than when two atoms of hydrogen are replaced by a bivalent substituent.

Each of the diamino-bases studied has been coupled with five acid compounds, namely, H-acid, chromotropic acid, Nevile and Winther's acid, resorcinol, and naphthoic acid. The resulting compounds have not been analysed, but were directly utilised for dyeing tests. The colours obtained are detailed in tabular form; they act as substantive colours for cotton, and dye wool from acid solutions.   E. F. A.

Thiophenols. III. *pp'*-**Azophenyl Methyl- and** *pp'*-**Azophenyl Ethyl-sulphide.** KURT BRAND and ADOLF WIESING (*Ber.*, 1913, **46**, 820—829).—The authors have extended their previous work on *pp'*-azophenyl methyl sulphide (A., 1912, i, 666), and have investigated the corresponding ethyl derivative.

A concentrated aqueous solution of sodium hydroxide and sodium sulphide is gradually added to a boiling alcoholic solution of di-*p*-nitro-diphenyl disulphide. From the cooled reaction mixture, the *sodium* derivative of *p*-nitrophenyl mercaptan, $C_6H_4O_2NSNa,2H_2O$, separates in golden leaflets, which decompose when heated slightly above 100°. The salt dissolves in water, forming a yellow solution, which, on addition of acid, becomes colourless and deposits *p*-nitrophenyl mercaptan. The solution absorbs oxygen with the formation of the disulphide. When warmed with an excess of ethyl bromide, the above sodium salt is transformed into *p*-nitrophenyl ethyl sulphide, m. p. 48° (Blanksma, A., 1902, i, 282, gives 40°; L. Gattermann, 44°). pp'-*Azoxyphenyl ethyl sulphide*, $ON_2(C_6H_4·SEt)_2$, is obtained when a methyl-alcoholic solution of p-nitrophenyl ethyl sulphide is added to a boiling solution of sodium methoxide in methyl alcohol. It forms pale yellow needles, m. p. 97—98°. A sulphinium compound could not be obtained from it by the action of methyl sulphate.

pp'-*Hydrazophenyl ethyl sulphide*, m. p. 76°, is obtained in the same manner as the corresponding methyl compound (*loc. cit.*). In alkaline alcoholic solution it is more readily oxidised by air than the

latter compound, and forms pp'-*azophenyl ethyl sulphide*. m. p. 132°. Treatment with concentrated hydrochloric acid transforms *pp'*-hydrazophenyl ethyl sulphide into p-*aminophenyl ethyl sulphide hydrochloride*, which readily gives up a portion of the hydrogen chloride. The free base, obtained from the hydrochloride by means of ammonia, has b. p. 165°/12 mm. (compare Auwers and Beger, A., 1894, i, 466; Monier-Williams, T., 1906, **89**, 278; Gattermann, A., 1912, i, 986). p-Acetylaminophenyl ethyl sulphide, m. p. 116°, is obtained by shaking an aqueous solution of p-aminophenyl ethyl sulphide hydrochloride with sodium acetate and acetic anhydride, or by boiling the free base with the same reagents.

pp'-Azophenyl ethyl sulphide, $N_2(C_6H_4\cdot SEt)_2$, orange leaflets, m. p. 132°, is obtained by reduction of p-nitrophenyl ethyl sulphide by means of zinc and sodium hydroxide and oxidation of the hot, filtered solution by passing air through it. With mineral acids and strong organic acids it yields intensely blue solutions. The crystalline *hydrochloride* and *trichloroacetate* could not be obtained in the pure state, as they decompose during filtration. The *sulphate*,

$$C_{16}H_{18}N_2S_2,2H_2SO_4,$$
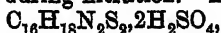
green metallic needles, is obtained by the addition of sulphuric acid to a solution of pp'-azophenyl ethyl sulphide in glacial acetic acid. The following double salts have been obtained : $C_{16}H_{18}N_2S_2,HCl,HgCl_2$, dark violet needles; $C_{16}H_{18}N_2S_2,HCl,FeCl_3$, green leaflets;

$$[C_{16}H_{18}N_2S_2,HCl]_2,FeCl_3,$$
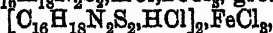
dark green needles; $C_{16}H_{18}N_2S_2,HCl,SnCl_4$, green leaflets;

$$[C_{16}H_{18}N_2S_2,HCl]_2SnCl_4,$$
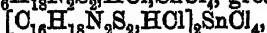
dark green needles. They were prepared by mixing pp'-azophenyl ethyl sulphide with the metallic chloride in hot glacial acetic acid solution, addition of hydrochloric acid being necessary in the first, third, and fifth cases. They are immediately decomposed by water.

When pp'-azophenyl ethyl sulphide is heated with methyl sulphate and the reaction mixture treated with alcohol, light red crystals, m. p. 158°, are obtained. The aqueous solution yields, on addition of potassium iodide, a sulphinium iodide, m. p. 158—160°, analyses of which gives results from which the authors conclude that the substance is pp'-azophenyldimethylsulphinium iodide. The discrepancy between the m. p. now found and that previously given (174—175°, *loc. cit.*) is attributed to impurity of the specimen.

In extension of their previous work, the authors have prepared the double *salt*, $(C_{14}H_{14}N_2S_2,HCl)_2SnCl_4$, green needles by the action of stannic chloride and hydrochloric acid on a solution of pp'-azophenyl methyl sulphide in glacial acetic acid. They also find that pp'-azophenyldimethylsulphinium methyl sulphate is more conveniently prepared by heating p'-azophenyl methyl sulphide and methyl sulphate for an instant at the boiling point and treatment of the resulting product with alcohol. When this salt is treated with sodium hydroxide, it forms a new *compound*, $C_{18}H_{20}O_8N_2S_4$, investigation of which is not yet completed.   H. W.

The Lakes of Hydroxylic Dyes. RICHARD MÖHLAU (*Ber.*, 1913, **46**, 443—456).—[With JOHANNES MAETZEL]—A brief account is first

given of previous investigations of the compounds of dyes with mordants.

A number of compounds were prepared from various metallic mordants and hydroxylic dyes by precipitation. For the production of simple lakes derived from tervalent metals, solutions of a salt of the metal and of the potassium derivative of the dye were mixed. In order to obtain more complex lakes containing both tervalent and bivalent metals, the tervalent metal derivative was first prepared, and its solution in ammonium hydroxide was then treated with a solution of an equivalent amount of the salt of the bivalent metal (compare Liechti and Suida, A., 1884, 794; 1885, 315; Liebermann and Michaelis, A., 1895, i, 108, 671; Biltz, A., 1906, ii, 78).

The fact that the lakes with the tervalent metals will dissolve readily in ammonium hydroxide indicates that the metallic atom is attached to hydroxylic oxygen, producing phenolic salts; the further introduction of the bivalent metallic atoms is then due to replacement of the hydrogen of the carboxyl or remaining hydroxyl group.

The following lakes of alizarin with tervalent metals were prepared, of the type $Me'''(C_{14}H_7O_4)_3$: *aluminium*, dark brown powder; *chromium*, yellow powder; *iron*, bluish-black powder. These could give calcium derivatives of the general formula $Me_2'''Ca_3(C_{14}H_6O_4)_6$; *aluminium calcium*, violet-brown; *chromium calcium*, deep violet; *iron calcium*, bluish-violet.

Of *p*-nitrobenzeneazosalicylic acid (the acid of alizarin-yellow-R), the following lakes were obtained with tervalent metals of the general formula

$$[NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot O \cdot]_3M''':$$

aluminium, red; *chromium*, brown; *iron*, chocolate. These gave calcium derivatives of the general formula

$$\left(NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3 {<}_{\;O}^{CO_2}{>}\right)_6 Ca_3Al_2:$$
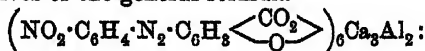
aluminium calcium, brownish-red; *chromium calcium*, brown; *iron calcium*, brownish-black.

The simple tervalent metallic lakes are more stable towards dilute acid and alkali than the more complex lakes containing two metals; of the latter, the aluminium calcium lakes are most stable and the iron calcium least, and those of alizarin are more stable than the corresponding derivatives of *p*-nitrobenzeneazosalicylic acid.

Benzeneazonaphtholsulphonic acid, $N_2Ph \cdot C_{10}H_5(OH) \cdot SO_3H$, and azo-*o*-toluene-azonaphtholsulphonic acid,

$$C_6H_4Me \cdot N_2 \cdot C_6H_3Me \cdot N_2 \cdot C_{10}H_5(OH) \cdot SO_3H,$$
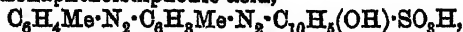
give unstable *chromium* lakes, brownish-red and claret-red respectively, which are decomposed by dilute alkali or mineral acid; they are consequently regarded as being normal chromium salts and not phenolic derivatives. Complex lakes containing two metals could not be prepared from them.   D. F. T.

Preparation of Acetyl Derivatives of Aminoazobenzene, its Homologues and Analogues. KALLE & Co. (D.R.-P. 253884).— Acetyl derivatives of aminoazobenzene and of the aminoazo-compound prepared from *o*-toluidine have been described previously; it is now

found that by prolonged heating with excess of the reagent, diacetyl derivatives are formed.

Diacetylaminoazotoluene exists in two modifications, long, reddish-yellow needles, m p. 65°, and in crystals, resembling potassium dichromate with m. p. 75°; *diacetylaminoazobenzene* forms long, thin plates, m. p. 103—104°.   F. M. G. M.

Density and Solution Volume of Certain Proteins. (Miss) HARRIETTE CHICK and CHARLES J. MARTIN (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 69—71).—From measurements of the density of casein, crystallised egg-albumin, crystallised serum-albumin and serum-globulin, and of the corresponding solution volumes in aqueous solution, it has been found that the density of the dissolved substance is in all cases greater than that of the free protein, the increase in density varying from 5 to 8%. In the case of serum-albumin and serum-globulin, the solution volume of the protein is independent of the concentration, whereas the contraction, which attends the dissolution of casein, diminishes as the concentration increases.   H. M. D.

The Amount of *l*-Tyrosine in Proteins and the Accuracy of its Estimation. EMIL ABDERHALDEN and DIONYS FUCHS (*Zeitsch. physiol. Chem.*, 1913, **83**, 468—473).—The colorimetric method proposed for the estimation of *l*-tyrosine by Folin and Denis (A., 1912, ii, 1012) is shown to include other amino-acids, and to be untrustworthy. It is possible by crystallisation to separate completely the tyrosine from the products of protein hydrolysis, particularly when the necessary concentration of the liquids is effected under reduced pressure. Most of the published determinations of tyrosine in proteins have been made with insufficient care.   E. F. A.

Colloidal Solutions. I. Certain Metallic Peptonates. EMANUELE PATERNÒ and FLORENTIN MEDIGRECEANU (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 65—68).—Solutions of iron, copper, zinc, and barium peptonate were subjected to prolonged dialysis, and after making up the volumes of the dialysed and residual solutions to the volume of the original solutions, measurements were made of the freezing point, total solids, ash, total nitrogen, and metal for each portion, the data being compared with the corresponding numbers for the original solutions. The observations seem to show that the substances formed by combination of peptone with the metal are, at any rate in the case of iron and copper, of colloidal nature.

H. M. D.

Porphyrinogen. HANS FISCHER and ERICH BARTHOLOMAUS (*Ber.*, 1913, **46**, 511—514).—By the action of a mixture of glacial acetic acid and hydrogen iodide in presence of phosphonium iodide on hæmin in the cold, a colourless, crystalline reduction product, $C_{33}H_{42}O_4N_4$, of high molecular weight is obtained. This is termed porphyrinogen in view of its ready conversion into a red product having the spectroscopic properties of porphyrin.

Sodium methoxide acts on porphyrinogen forming phyllopyrrole;

also a porphyrin, of which the hydrochloride crystallises in centrically grouped needles—probably mesoporphyrin.

On oxidation, porphyrinogen yields methyl ethylmaleinimide and hæmatic acid.

The colourless porphyrinogen behaves as a sensibilising agent when injected into mice exposed to light rays.   E. F. A.

Pepsin. II. SERAFINO DEZANI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 194—200. Compare A., 1910, i, 449).—The pepsin prepared according to the method previously described contains very little chlorine, and the author now finds that by suitable purification this element can be removed almost completely without diminishing the activity of the product. It appears, therefore, that the statements of previous authors that chlorine is a constituent of the substance are incorrect.   R. V. S.

Some Properties of Koji-diastase. G. KITA (*J. Ind. Eng. Chem.*, 1913, **5**, 220—222).—It has been generally assumed that koji (a culture of *Aspergillus oryzae* on steamed rice) contains two different saccharifying enzymes only, namely, amylase and glucase, and that the dextrose present in a liquid saccharified by means of koji is produced by these two enzymes. Comparative experiments on starch and maltose showed, however, that more dextrose was produced from the starch than from maltose, and the author concludes that koji contains a third enzyme which produces dextrose directly from starch without the aid of glucase.

Sodium chloride has a protecting action on koji-diastase when heated, but not on malt-diastase, whilst sodium phosphate, asparagine, and sulphuric acid impair its activity more quickly. The inhibitory action of the sodium chloride depends on the concentration of the diastase; in a dilute solution of the enzyme it is very marked. but not in a concentrated solution. The activity of koji-diastase may be conserved in brine solution for a long period.   T. S. P.

The Reversibility of the Ferment Action of Emulsin. ÉMILE BOURQUELOT and J. COIRRE (*Compt. rend.*, 1913, **156**, 643—646; *J. Pharm. Chim.*, 1913, [vii], **7**, 236—240. Compare A., 1912, i, 928; this vol., i, 212).—The state of equilibrium attained during the synthesis or hydrolysis of a glucoside in alcoholic solution under the influence of emulsin is independent of the amount of emulsin used and depends solely on the proportions of the components of the glucoside in the solution. The action is thus a true reversible reaction, the only effect of varying the concentration of the emulsin being to vary the rate at which equilibrium is reached.   W. G.

Hydrolysis of Amygdalin Under the Influence of Emulsin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1913, **251**, 85—89).—Krieble's observation (A., 1912, i, 482) that certain kinds of emulsin react with amygdalin to give *l*-benzaldehydecyanohydrin is confirmed, and a series of experiments has been made to determine the mode of formation of the latter. It is shown that a portion of the benzaldehyde and

hydrogen cyanide which result from the gradual breaking down of amygdalin through mandelonitrile-glucoside and *d*-benzaldehyde-cyanohydrin re-combine to form *i*-benzaldehydecyanohydrin, and if an emulsin such as that from cherry kernels, which is very rich in *d*-oxynitrilase, is used, hydrolysis of the *d*-component of the inactive cyanohydrin ensues, *l*-benzaldehydecyanohydrin being left unaltered.

T. A. H.

Distribution of Emulsin-like Enzymes. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1913, · 251, 56—84).—The work done in recent years on "emulsin" shows that the latter may include different enzymes depending on its origin (A., 1910, i, 800 ; Armstrong and others, A., 1912, i, 816). The author has, therefore, investigated a large number of plants, particularly those which are known to be cyanogenetic, with a view to ascertaining which of the ordinary components of "almond emulsin" they contain. For this purpose the mixture of enzymes prepared from the plant was mixed with (1) a solution of amygdalin, (2) a mixture of benzaldehyde and hydrocyanic acid (A., 1909, i, 74, 622), and (3) *dl*-benzaldehydecyanohydrin (Feist, A., 1909, i, 589), and the products of the reaction, if any, investigated. The results are described in detail in the original, and are also tabulated for convenience of reference. The following points of special interest are recorded. Enzymes capable of producing asymmetric synthesis or decomposition (reactions 2 and 3 above) are widespread in plants, although less so that those capable of decomposing amygdalin ; this apparent difference may, however, be due to the fact that enzymes of the last-mentioned type are easier to detect by means of their product of reaction. Enzymes of these types may occur in plants which do not yield hydrogen cyanide, but in such cases they are not found in the leaves. These enzymes are not identical with those which decompose amygdalin, since in certain cases, such as *Hydnocarpus Wightiana* seeds, *Pangium edule* seeds, and *Prunus laurocerasus* leaves, negative results were obtained in reaction (1) and positive results with (2) and (3). Similarly, in other cases positive results were obtained for reaction (2) and negative results for reaction (3). An enzyme preparation from the seeds of *Taraktogenos Blumei* furnished in reaction (2) *l*-benzaldehydecyanohydrin instead of the *d*-isomeride furnished by enzymes derived from plants of the order Prunaceæ ; these seeds therefore appear to contain a *l*-oxynitrilese, which may also be present in the flowers of *Achillea millefolium*. No enzyme capable of producing optically active nitriles from ketones and hydrocyanic acid was observed. The enzyme of *Taraktogenos Blumei* is soluble in brine, but not in water. T. A. H.

Oxydases. VI. Tyrosinase is also a Deamidising Enzyme. ROBERT CHODAT and K. SCHWEIZER (*Arch. Sci. phys. nat.*, 1913, 35, 140—147. Compare A., 1912, ii, 399, 611).—It has been shown previously that for the completion of the colour reaction between tyrosinase and *p*-cresol, the presence of an amino-acid is necessary. It is now proved that tyrosinase has a deamidising action on glycine, which it converts into carbon dioxide, ammonia, and formaldehyde.

f f 2

The change is greatly facilitated by the addition of lime water. The formation of formaldehyde is identified by means of Rimini's reagent (phenylhydrazine hydrochloride and potassium ferrocyanide), that of ammonia by means of Nessler's and Trillhat's reagents. The interaction of *p*-cresol, glycine, and tyrosinase is prevented by the addition of calcium hydroxide; in its absence the blue coloration is obtained, and formaldehyde and ammonia are detected amongst the products of reaction.

With alanine and tyrosinase, acetaldehyde is formed in place of formaldehyde. Benzaldehyde is obtained from phenylglycine and tyrosinase.

The presence of formaldehyde in plant tissues does not necessarily indicate photo-synthesis. Attention is drawn to the parallelism between the action of tyrosinase and of hydrogen peroxide on glycine (compare Dakin, A., 1906–1911).   E. F. A.

Preparation of Derivatives of Nitrohydroxy- and Amino-hydroxy-arylarsinic Acids Containing Sulphur. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 253757).—When an alkaline solution of 3-nitro-4-hydroxyphenylarsinic acid is saturated with hydrogen sulphide at the ordinary temperature, it gives rise to *nitrohydroxyphenylarsenosesquisulphide*, $[NO_2 \cdot C_6H_3(OH) \cdot As]_2S_3$, which crystallises from xylene in hard, yellow, nodular crystals, m. p. 160° (about).

Compounds obtained by the action of sodium sulphide on 3-nitro-4-hydroxyphenylarsinic acid (a pale brown powder), of hydrogen sulphide on 3-amino-4-hydroxyphenylarsinic acid, and on its hydrochloride are also described.   F. M. G. M.

Aromatic Arsenic Compounds. IV. Preparation of 3-Nitro 4-dimethylaminophenylarsinic Acid and of 3-Nitro-4-hydroxyphenylarsinic Acid. P. KARRER (*Ber.*, 1913, **46**, 515—517).—*p*-Dimethylaminophenylarsinic acid is readily nitrated on solution in a mixture of acetic and nitric acids. When the mononitrodimethylaminophenylarsinic acid, $NO_2 \cdot C_6H_3(NMe_2) \cdot AsO_3H_2$, is warmed with sodium hydroxide, it is converted into 3-nitro-4-hydroxyphenylarsinic acid (Benda and Bertheim, A., 1911, i, 63), which in turn, when reduced, gives rise to the base,

$$NH_2 \cdot C_6H_3(OH) \cdot As \vdots As \cdot C_6H_3(OH) \cdot NH_2,$$

corresponding with salvarsan.

When 3-nitro-4-dimethylaminophenylarsinic acid is similarly reduced, tetramethyltetra-aminoarsenobenzene,

$$NMe_2 \cdot C_6H_3(NH_2) \cdot As \vdots As \cdot C_6H_3(NH_2) \cdot NMe_2,$$

is obtained. This compound has no curative action towards mice infected with trypanosomes.

3-Nitro-4-dimethylaminophenylarsinic acid crystallises in lustrous, yellow needles.

The *hydrochloride* of *tetramethyltetra-aminoarsenobenzene* is a yellowish-white powder.   E. F. A.

Aromatic Arsenic Compounds. III. Triazoarylarsinic Acids and Some of their Derivatives. P. KARRER (*Ber.*, 1913, **46**, 249—255).—Some triazophenylarsinic acids have been prepared

by the addition of sodium azoimide to the corresponding diazotised amines. They are very stable towards dilute sulphuric acid, and cannot be hydrolysed to aminophenols, but the *o*-nitrated azoimides give up nitrogen when heated and undergo rearrangement to *o*-dinitroso-compounds (compare Zincke and Schwarz, A., 1899, i, 751), which can be readily condensed with dimethylaniline to phenazine derivatives.

p-*Triazophenylarsinic acid*, $N_3 \cdot C_6H_4 \cdot AsO_3H_2$, from *p*-aminophenylarsinic acid, crystallises in stout, white crystals, and gives a *monosodium* salt. 3-*Iodo-4-triazophenylarsinic acid* forms white crystals, and 3-*nitro-4-triazophenylarsenic oxide*, $N_3 \cdot C_6H_3(NO_2) \cdot AsO$, prepared from 3-nitro-4-aminophenylarsenic dichloride, which, in turn, is obtained from the arsinic acid, is a yellow, crystalline powder. 3-*Nitro-4-triazophenylarsinic acid*, a yellow, crystalline powder, loses nitrogen at 75°, and changes into 3 : 4-*dinitrosophenylarsinic acid*, $C_6H_3(NO)_2 \cdot AsO_3H_2$; this condenses with dimethylaniline to form 2-(or 3-)-*dimethylaminophenazine-7-arsinic acid*, $C_{14}H_{12}O_3N_3As$, as a blue dye which is very soluble in acetic acid and in sodium hydroxide. 2-*Nitro-3-triazophenylarsinic acid* also condenses with dimethylaniline, but 2-(or 3-)-*dimethylaminophenazine-8-arsinic acid* is insoluble in sodium hydroxide and has a reddish tinge. 3-Nitro-4-triazophenylarsinic acid can also be condensed with *o*-phenylenediamine in glacial acetic acid, when the *acetate* of 2 : 3 - *diaminophenazine* - 7 - *arsinic acid* separates as a brick-red powder. The free base (annexed formula) is yellow, gives a *diacetyl* derivative as a yellowish-brown powder, and when treated with sodium nitrite and acetic acid deposits the *compound*,

$$AsO_3H_2 \cdot C_6H_3 {\ll}^N_N{>} C_6H_2 {<}^{NH}_{-N} {>} N,$$
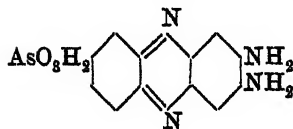
in the form of a brown powder.

J. C. W.

Iso- and Hetero-poly-salts. VIII. Alkylarsinomolybdates. ARTHUR ROSENHEIM and ROBERT BILECKI (*Ber.*, 1913, **46**, 539—557. Compare A., 1911, i, 109, 265; ii, 116, 612; this vol., ii, 59).—In order to examine further the extension of Werner's co-ordination theory to poly-acids by Miolati and Pizzighelli (A., 1908, ii, 595), the authors have prepared a series of alkylarsinomolybdates. They find that the number of MoO_4 or Mo_2O_7 radicles which unite with the alkylarsenates to form complex compounds is intimately connected with the number of oxygen atoms in the arsinate anion, and diminishes as the number of alkyl radicles present increases. The basicity of the hetero-poly-acids so formed is either equal to, or, generally, higher than, that of the corresponding alkylarsinates. Normal hetero-poly-salts could not in all cases be obtained. This is attributed to the fact that the acids contain weakly electro-negative complex ions which are hydrolysed on neutralisation of the solutions. The composition of the hetero-poly-salts is found to depend on the electro-affinity of the central atom ; more powerfully electronegative anions, such as the phenylarsinate- and *p*-hydroxyphenylarsinate-anions unite with MoO_4

radicles, whilst the weaker electronegative anions, such as the dialkylarsinate-anion, unite with Mo_2O_7 radicles.

The authors' experiments on solutions of cacodylic and molybdic acids agree with those of Miolati (*loc. cit.*). The latter, however, found breaks in the graph for the electrical conductivity of solutions of molybdic and methylarsinic acids at the proportions

$$AsMeO_3H : MoO_3 = 2 : 5 \text{ and } 1 : 10.$$
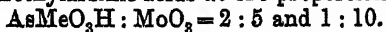
Since these figures did not agree with those obtained by the authors, the latter have plotted Miolati's graph on a larger scale, and find that it is not exact, somewhat weak breaks actually occurring at the proportions $AsMeO_3H : MoO_3 = 1 : 6$ and $1 : 9$. The corrected result agrees with the authors' determinations.

A boiling aqueous solution of sodium methylarsinate was saturated with molybdic acid, and, after concentration, an excess of guanidinium chloride was added. Two *guanidinium* salts were thereby obtained, the less soluble of which was composed of rectangular plates having the formula $(CN_3H_6)_2[AsMe(Mo_2O_7)_3],11H_2O$, whilst the more soluble salt consisted of white needles having the composition

$$(CN_3H_6)_8H_2\begin{bmatrix} \overset{Me}{As(Mo_2O_7)_4} & \overset{Me}{(Mo_2O_7)_4As} \\ -Mo_2O_7- \end{bmatrix},8H_2O.$$
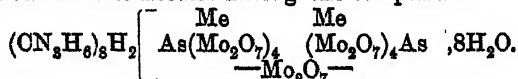
In alkaline solution only the latter salt was obtained.

Sodium phenylarsinate, when similarly treated, also yielded two *guanidinium* salts. The less readily soluble salt, white leaflets,

$$(CN_3H_6)H[AsPh(MoO_4)_3],H_2O,$$
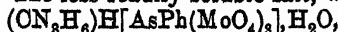
did not yield a neutral salt when boiled with excess of guanidinium carbonate. The more soluble salt, long, white needles,

$$(CN_3H_6)_5H_5\begin{bmatrix} AsPh(MoO_4)_4 & (MoO_4)_4AsPh \\ \underline{\qquad MoO_4-- \qquad} \end{bmatrix},6H_2O,$$
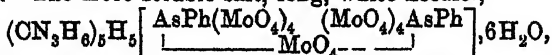
behaved according to conductivity measurements as the salt of a normal pentabasic substance. The hydrogen atoms could not be replaced by base in aqueous solution. In faintly alkaline solution, the more soluble salt was exclusively formed. When the latter salt was suspended in water and gently heated with guanidinium carbonate, the *salt*, $(CN_3H_6)_6H_2\begin{bmatrix} AsPh(MoO_4)_3 & (MoO_4)_3AsPh \\ OH & MoO_4 & OH \end{bmatrix},4H_2O$, was obtained. Precisely similar salts were obtained from those derivatives of phenylarsinic acid which did not form too powerfully electronegative anions; thus, from sodium *p*-aminophenylarsinate, the *guanidinium* salt, $(CN_3H_6)_2\begin{bmatrix} As\dfrac{C_6H_4 \cdot NH_2}{(MoO_4)_3} \end{bmatrix},5H_2O$, pale yellow leaflets, was prepared, whilst sodium *p*-hydroxyphenylarsinate yielded a *guanidinium* salt, $(CN_3H_6)_2\begin{bmatrix} As\dfrac{C_6H_4 \cdot OH}{(MoO_4)_3} \end{bmatrix},2H_2O$, white needles, and also a more soluble *salt*, crystallising in small plates. A complex salt derived from *p*-carboxyphenylarsinic acid could not be isolated.
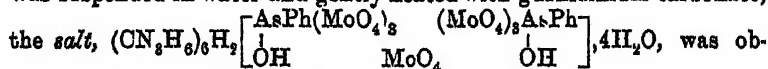
Sodium cacodylate, when treated with molybdic acid and subsequently with guanidinum chloride, gave the *guanidinium* salt, $(CN_3H_6)_2\begin{bmatrix} AsMe_2(Mo_3O_7)_2 \\ (OH)_3 \end{bmatrix}$, colourless, anhydrous plates. The micro

crystalline *lead, copper,* and *silver* salts were also prepared. The *potassium* salt, prepared from potassium cacodylate in the usual manner, formed microscopic needles of the formula $K_2H\begin{bmatrix} AsMe_2(Mo_2O_7)_2 \\ (OH)_2 \end{bmatrix}$. The corresponding *barium* salt was obtained by the action of barium chloride on the sodium salt.

In a similar manner, the *guanidinium* salt,

$$(CN_3H_6)_2H\begin{bmatrix} AsPh_2(Mo_2O_7)_2 \\ (OH)_2 \end{bmatrix},H_2O,$$
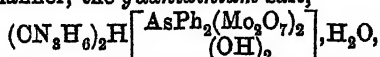
white, hexagonal plates, was obtained from sodium diphenylarsinate.

An aqueous solution of trimethylarsonium hydroxide was saturated with molybdic acid at its boiling point. The solution, when concentrated, deposited a yellow, microcrystalline substance,

$$AsMe_3(OH)_2H_3\begin{bmatrix} AsMe_3(Mo_2O_7)_2 \underset{-O-}{} (Mo_2O_7)_2AsMe_3 \end{bmatrix},3H_2O.$$
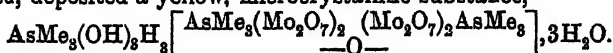
When, however, guanidinium chloride was added to the above solution before the latter compound had separated, the *guanidinium* salt,

$$(CN_3H_6)_3H_3\begin{bmatrix} AsMe_3(Mo_2O_7)_2 \underset{-O-}{} (Mo_2O_7)_2AsMe_3 \end{bmatrix},$$
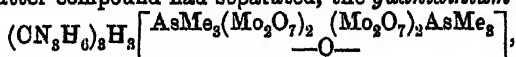
was obtained as microscopic, white plates.

When triphenylarsine oxide was dissolved in boiling aqueous sodium molybdate solution and the latter acidified by gradual addition of hydrochloric acid, a yellow, amorphous *substance,* $\begin{bmatrix} As\dfrac{Ph_3}{Mo_2O_7} \end{bmatrix}$, was obtained.

H. W

Preparation of Organic Arsenic Compounds. HEINRICH BART (D.R.-P. 254345. Compare this vol., i, 115).—When solutions of *iso*-diazo-compounds react with diarylarsenious oxides (or acids) they give rise to triarylarsine hydroxides or oxides :

$$RN{:}NOH + R_2As{\cdot}OH = N_2 + R_3AsO + H_2O.$$
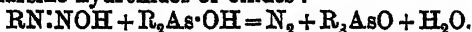
A 10% solution of sodium *p*-nitro*iso*diazobenzene is slowly treated with dinitrodiphenylarsenious acid and sodium hydroxide (1 mol.) ; on slowly heating to 75—80°, nitrogen is evolved, and on the addition of acid the trinitrotriphenylarsine oxide separates as a brown precipitate.

The required *dinitrodiphenylarsenious acid* is obtained by the careful reduction of dinitrodiphenylarsinic acid with hydrogen iodide in acetic acid solution ; when heated it decomposes energetically without fusion.
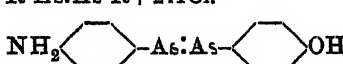
F. M. G. M.

Preparation of Unsymmetrical Arseno-compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 253226).— Unsymmetrical aromatic arseno-compounds have previously been prepared (this vol., i, 116), and this reaction has now been extended to the case of compounds containing both aliphatic and aromatic residues.
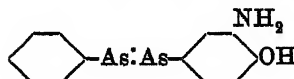
3-*Amino*-4-*hydroxybenzenearsenomethane* (annexed formula), a yellow powder soluble in dilute acids and alkaline hydroxides, is obtained when a methyl-alcoholic solution of 3-amino-4-hydroxyphenylarsenious oxide is treated with a similar solution of methyl arsenious oxide (A., 1906, i, 488), water added, and the mixture reduced with sodium hyposulphite.

$$CH_3{\cdot}As{:}As\!\!\left\langle\!\!\!\begin{array}{c} NH_2 \\ \\ OH \end{array}\!\!\!\right.$$
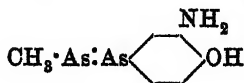
One or both of the arsenious oxides in the foregoing reaction can be replaced by the corresponding acids, in which case the reduction is carried out with stannous chloride and hydrogen iodide at $-10°$ to $-20°$.   F. M. G. M.

Preparation of Aromatic Arseno-compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 254187. Compare A., 1909, i, 347; 1910, i, 148).—When aromatic arsinic acids are reduced in strongly acid solution they give rise to primary arsines of general formula $R \cdot AsH_2$ ($R = $ aryl), which can be condensed with aryl-arsenious oxides or haloids to yield aromatic arseno derivatives (this vol., i, 117): $R \cdot AsH_2 + R \cdot AsO = R \cdot As : As \cdot R + H_2O$; $R \cdot AsH_2 + R \cdot AsCl_2 = R \cdot As : As \cdot R + 2HCl$.

$NH_2 \langle \quad \rangle - As:As - \langle \quad \rangle OH$ *4 - Amino - 4′ - hydroxyarsenobenzene* (annexed formula), a yellow powder, decomposes at about $200°$; 3-amino-4-hydroxy-4′-glycylarsenobenzene (this vol., i, 116) darkens at $120°$ and decomposes violently at $150°$, and *3-amino-4-hydroxyarsenobenzene*

$\langle \quad \rangle - As:As - \langle \quad \rangle OH$ (annexed formula) forms a yellow powder.
                                      Other compounds mentioned as being prepared by this method are 4 : 4′-diamino-arsenobenzene and 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene.   F. M. G. M.

Preparation of Aromatic Stibinic Acids. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 254421. Compare Trans., 1911, 99, 2286).—Phenylstibinic acid has previously been prepared (Hasenbäumer and others) by a somewhat complicated series of reactions; the following simple method is now described.

Antimony trioxide (140 parts) is dissolved at the ordinary temperature in 764 parts of hydrochloric acid (D 1·123), treated with sodium hydroxide (600 parts) in water (3000 parts), and rapidly cooled to $0°$, when part of the sodium antimonite separates. A solution of anilino-diazonium sulphate (prepared from 93 parts of aniline and 147 parts of sulphuric acid) is then rapidly stirred in, either with or without the addition of copper paste; after some hours the mixture is carefully neutralised with sulphuric acid, filtered, and the phenylstibinic acid precipitated by the addition of hydrochloric acid. To purify the product from antimony trioxide it is dissolved in hot hydrochloric acid (D 1·123), and the solution saturated with solid ammonium chloride, when on cooling *phenylstibinic oxychloride* separates in glistening leaflets; this is isolated, decomposed with sodium carbonate, and the pure phenylstibinic acid precipitated with hydrochloric acid. As thus prepared, phenylstibinic acid is stable at $250°$ (Hasenbäumer gives decomp. point $200°$).

p-*Hydroxyphenylstibinic acid* and p-*acetylaminophenylstibinic acid* are similarly prepared from p-aminophenol and monoacetyl-p-phenylene diamine respectively; the *sodium* salt of the latter dissolves in water with a neutral reaction. p-*Aminophenylstibinic acid*, obtained by the hydrolysis of the foregoing acid, combines readily with aldehydes

(salicylaldehyde) to furnish hydroxybenzylidene derivatives or on diazotisation gives rise to a red azo-derivative with alkaline β-naphthol.

F. M. G. M.

Preparation of Nuclear Substituted Mercury Derivatives of Aromatic Hydroxy-acids CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 255030).—The following therapeutically active organic derivatives of mercury have now been prepared.

Mercurydisalicylic acid, $Hg[C_6H_3(OH)\cdot CO_2H]_2$, a colourless powder, insoluble in water, is obtained by the reduction of *o*-hydroxymercurisalicylic anhydride with sodium formaldehydesulphenate, and is employed in the form of its neutral *alkali* salts.

Mercury-bis-sulphosalicylic acid, also employed in the form of its *sodium* salt, is similarly prepared from sodium mercurisulphosalicylate.

Mercury-bis-arsenosalicylic acid, a colourless powder, is obtained from mercury arsenosalicylic acid.

*Sodium mercuri-bis-*2-*naphthol-*3 : 6 *disulphonic acid* and *mercury-bis-*4-*hydroxy-*m-*tolyl-*1-*arsinic acid* are also employed in the form of their crystalline *sodium* salts. F. M. G. M.

Physiological Chemistry.

The Influence of Phosphorus on Respiratory Metabolism. OTTO HIRZ (*Zeitsch. Biol.,* 1913, **60**, 187—310).—The respiratory exchange in rabbits sinks regularly during inanition. On the second day the nitrogenous output and the urea rise and remain at a constant level as the organ protein is utilised. In fat animals the consumption of the organ protein is delayed. In phosphorus poisoning the decrease in respiratory metabolism is not a specific effect of the poison on metabolism, but is secondary to pain and other symptoms produced. With small doses there is a slight increase in respiratory activity. The nephritis produced lessens the output of nitrogen, but in fat animals this is preceded by an increase. Carbohydrate metabolism is unaffected. The combustion of fat increases. No support is found for the hypothesis that the fat which appears in the organs ("fatty degeneration") is of protein origin. The permeability of the blood vessels is greatly increased.

W. D. H.

The Coagulation of Blood. WILHELM CRAMER and HAROLD PRINGLE (*Quart. J. expt. Physiol.,* 1913, **6**, 1—12).— If oxalate plasma is filtered through a Berkefeld filter, it does not clot when calcium chloride is added to it. This is due to removal of the platelets, which are still present in oxalate plasma prepared in other ways. The addition of calcium chloride to ordinary oxalate plasma liberates thrombokinase (Howell's thromboplastin) from the

platelets. Soluble calcium salts, in addition to this primary effect on the platelets, contribute also to the formation of fibrin under the influence of the substance liberated from the •platelets. In paraffined tubes blood remains fluid because the platelets are intact; when transferred to glass tubes the platelets in contact with the glass disintegrate, and clotting ensues. The phenomena described by Nolf as "thromboplastic agencies" and "centres of coagulation" are due to the presence of platelets. Plasma free from platelets are not susceptible to the action of "thromboplastic agencies."

W. D. H.

The Plasma of Propeptone. HENRI STASSANO (*Compt. rend.*, 1913, **156**, 735—738).—The plasma obtained after the intravenous injection of propeptone differs in several respects from plasma, to which salts have been added. The first is coagulated when diluted either with distilled water or even with a solution of an anti-coagulating salt, whilst the latter is only coagulated on dilution with water. The plasma of propeptone behaves thus as a mixture of serum and fibrinogen in decalcified solution. The coagulation of propeptone plasma on dilution is unaffected by change in temperature, whilst that of the saline plasma is checked by cooling. In tubes coated with paraffin wax, the former plasma coagulates on dilution with only a slight retardation, whilst the latter remains indefinitely liquid. The coagulating power of propeptone plasma towards the peritoneal serum from a horse is greater at the moment of dilution than two hours afterwards, whilst that of saline plasma steadily increases after dilution. These differences point to the fact that, whilst in the saline plasma the fibrin-ferment is in an inactive state, in the plasma of propeptone it is in the active state. W. G.

The Transference of the Digestion Products of Proteins from the Mother to the Fœtus. GIUSEPPE BUGLIA (*Biochem. Zeitsch.*, 1913, **48**, 362—372).—The distribution of nitrogen in the blood of the fœtus and mother in the case of dogs was determined both when digestion products had been injected into the jugular or femoral vein, and when either no injection had been made, or only saline had been administered. From the comparison of the various results obtained, the conclusion is drawn that protein digestion products can pass directly from the mother to the fœtus.

S. B. S.

The Influence of Nutrition on the Amylase Content of Human Saliva. O. LOVATT EVANS (*Biochem. Zeitsch.*, 1913, **48**, 432—447).—The amylase content (estimated by determining the amount of maltose produced from a given starch solution in a given time by Bertrand's method) increases after a meal. The increase commences twenty to thirty minutes after a meal, and lasts for two to three hours, when it reaches a maximum and then wanes. The activity remains then small until the next meal is taken. The content is not affected after mock feeding (mastication of food without swallowing). A meal of purely protein content does not

increase the amylase. The mechanism of the secretion can be explained by assuming that carbohydrates act on the mucous membrane of the stomach and produce a hormone. The increase in amylase content is to be ascribed principally to the saliva produced by the parotid gland, which has about four times the enzymatic activity of that of the remainder of the glands. The parotid, furthermore, produces about half the total volume of the saliva.

S. B. S.

The Behaviour of Plasteins in the Animal Body. I. The Relationships of Plasteins to Peptone Poisoning. ERICH VON KNAFFL-LENZ and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1913, **71**, 296).—If pepsin hydrochloric acid acts on a poisonous peptic digest, substances of higher molecular weight (plasteins) are formed which are not poisonous. The formation of plasteins in the body is regarded as protective. If the plasteins are again subjected to gastric action, poisonous products again arise; tryptic digestion is ineffective in this direction. The phenomenon is thus a reversible one. The final cleavage products of protein digestion are not poisonous. W. D. H.

Pancreatic Digestion. FRIEDRICH AUERBACH and HANS PICK (*Biochem. Zeitsch.*, 1913, **48**, 425—426).—Attention is called to the fact that, whereas natural pancreatic juice possesses the optimal hydroxyl ion concentration for lipoclastic or peptoclastic function, the digestion of proteins proceeds best in a medium more distinctly alkaline. This indicates that the preliminary digestion of proteins takes place for the most part in the stomach rather than in the intestine, the function of which is to digest the peptones. S. B. S.

Comparative Physiology of Digestion. VI. Cellulose and Cellulose-dissolving Enzymes in the Hepatopancreas of the Snail (Helix pomatia). JERZY STANISŁAW ALEXANDROWICZ (*Pflüger's Archiv*, 1913, **150**, 57—86).—Attention is directed to the two forms of crystalline cellulose, namely, those in plant sections, and the sphæro-crystals prepared *in vitro* by Gilson and Bütschli. The former have strong, doubly refracting properties; the sphæro-crystals are only feebly anisotropic. In plant membranes hemicelluloses are present, which increase their anisotropy. Crystallised cellulose is dissolved by the snail's hepatopancreas. Hence celluloses of different origin differ a good deal in solubility in the juice. It is suggested that the enzymes which dissolve cellulose and hemicellulose may be investigated microscopically in the study of the chemical composition of vegetable membranes. W. D. H.

The Synthetic Powers of the Organism of the Dog. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1913, **83**, 444—457) — The dog under observation was kept for three months on carbohydrate, fat, and the completely cleaved products of meat hydrolysis. It gained 10 kilograms in weight, and renewed its fur. Tryptophan and tyrosine are essential, and their absence is followed by untoward symptoms. Hopkins' view that tryptophan is essential for the formation of certain internal secretions is regarded as probable but unproven. W. D. H.

Action of Ammonium Salts, Glucosamine and Gelatin on the Nitrogen Balance. EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem*, 1913, **83**, 409—424).—Experiments similar to those previously carried out on dogs are now recorded on two pigs. On most days there was a loss of nitrogen; in this and some other details the results differ from those of Grafe on pigs. A further series of experiments on a dog yielded much the same results. This dog died of tetanus, which is attributed to tetanus spores in the gelatin given. This is the first recorded instance of tetanus infection through the alimentary tract.

<div align="right">W. D. H.</div>

Utilisation of Calcium and Phosphoric Acid Compounds by the Animal Organism. GUSTAV FINGERLING (*Landw. Versuchsstat*, 1913, **79**—80, 847—870. Compare *ibid.*, **75**, 1).—Feeding experiments in which goats received, in addition to straw, blood nuclein, starch, and oil, the following substances as sources of phosphorus: phytin, lecithin, casein, nuclein, nucleic acid, and disodium phosphate. The food was mixed with molasses to make it palatable.

The results showed that there is no essential difference in the utilisation of the different forms of phosphorus. The imperfect assimilation of the phosphoric acid of crude foods must, therefore, be due to other causes.

<div align="right">N. H. J. M.</div>

Comparative Investigations on the Content of Aminoacids in the Different Constituent Parts of the Nervous System. II. The Amino-acids of the Grey and White Substance of the Brain. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1913, **83**, 425—440).—The results of the analyses of grey and white brain matter are given in tables, together with the methods used. The details relate to water, total nitrogen, ash, and various amino-acids.

<div align="right">W. D. H.</div>

The Action of the Diastatic Enzyme on the Glycogen within the Cells JULIUS GRODE and ERNST J. LESSER (*Zeitsch. Biol.*, 1913, **60**, 371—387).—The surviving liver and muscles of winter (glycogen-rich) frogs in oxygenated Ringer's solution lose little or none of their glycogen. The same was stated by Schiff in 1859. If the cells are destroyed mechanically, the glycogen disappears rapidly. The enzyme responsible for the change is considered to exist in the cells as a zymogen, which is converted into the active enzyme as the cells are killed.

<div align="right">W. D. H.</div>

The Behaviour of the Glycogen of the Frog in Anoxybiosis and Restitution. III ERNST J. LESSER (*Zeitsch. Biol.*, 1913, **60**, 388—398).—In the living summer frog (poor in glycogen) the anoxybiotic glycogen disappearance is about 50% in two hours at 20°. In restitution in the summer, contrary to what is seen in winter frogs, there is a well-marked new formation of glycogen. Under anoxybiotic conditions lasting two or three days, the

glycogen also is lowered by about 50%. Normal frog's blood contains no sugar when tested for by the method of Michaelis and Rona. In anoxybiosis the blood contains 0 07% sugar, and minute amounts may pass into the urine.   W. D. H.

Comparative Anatomy and Physiology of the Pituitary Body. Percy T. Herring (*Quart. J. expt. Physiol*, 1913, **6**, 73—108) —The pituitary bodies of the classes of vertebrates resemble one another in essential features. In elasmobranch fishes, however, the nervous lobe is absent.

No portion of the epithelial lobe in any case contained the active principles associated with the posterior lobe in mammalia. The *pars intermedia* by itself or the colloid matter separated from it have no specific effect on blood-pressure or kidney. The hormone which affects the mammary gland is obtainable from the skate's pituitary (which has no nervous lobe), and therefore appears to be a separate substance. It is still more abundant in the posterior (nervous) lobe in other animals; it is probable that it is a product of the epithelial lobe, and is stored in the *pars nervosa*. The latter is composed of modified ependyma and neuroglia cells permeated by a gelatinous substance containing fine granules and hyaline bodies. The granules are considered to be the representatives of the active principles of the nervous lobe; they are the products of the cells of the *pars intermedia* (in origin, a portion of the epithelial lobe); these are carried to, elaborated in, and stored by the *pars nervosa*.   W. D. H.

The Effects of the Administration of Extracts of the Pituitary Body and Corpus Luteum to Milch Cows. W. Gavin (*Quart J. expt. Physiol.*, 1913, **6**, 13—16).—Under conditions of farm practice, no commercial benefit arises from the administration to dairy cows of these glandular extracts, whether given by the mouth, under the skin, or intravenously. Intravenous injection of pituitary extract causes more milk to collect in the lower parts of the udder, but no alteration in the total quantity per diem, or in the quality of the milk, occurs.   W. D. H.

The Effect of Pituitary and Corpus Luteum Extracts on the Human Mammary Glands Edward A. Schäfer (*Quart. J. expt. Physiol.*, 1913, **6**, 17—20).—Observations on a woman of twenty eight nursing her second child show that injection of pituitary extract intramuscularly, produced a tingling sensation in the breasts, and an increased flow of milk. The effect was not lasting, and a long time elapsed before there was again enough milk to feed the child. The effect of similar injections of extract of the corpus luteum was doubtful.   W. D. H.

The Liberation of Ions and the Oxygen Tension of Tissues during Activity. Herbert E. Roaf (*Proc. Roy. Soc.*, 1913, *B*, **86**, 215—218).—A preliminary account of an investigation of muscle by various kinds of electrodes, and the results give evidence that

hydrogen and probably chlorine ions are liberated during the act of contraction. There is also a fall in oxygen tension.   W. D. H.

The Summation of Muscular Contractions. GEORGE R. MINES (*J. Physiol.*, 1913, **46**, 1—27).—Reasons are given for thinking that the liberation of acid in muscle as the result of excitation precedes the act of shortening and possibly causes it. When a second excitation can be produced before the first localised concentration of acid has had time to diffuse away, the result may be a summation of these localised concentrations, and so a greater effect on the contractile mechanism. Such an effect may, however, occur at a time when the general hydrogen ion concentration of the muscle is such that further increase tends only to diminish the power of the response of the muscle.   W. D. H.

The Energy Degraded in the Recovery Processes of Stimulated Muscles. ARCHIBALD V. HILL (*J. Physiol.*, 1913, **46**, 28—80). —A thermoelectric apparatus is described by which it is possible to estimate and record rapidly the rise of temperature of a muscle to within a millionth of a degree. The production of heat in a muscle excited in oxygen either by a single shock or a short tetanus continues for long periods after the mechanical response is over; but after the muscle has been kept in nitrogen for an hour there is no trace of heat production following the contraction; on being restored to oxygen this returns. Previous excitations or a prolonged tetanus, which diminish the oxygen tension in the muscle, lessen the heat production after the contraction. The "delayed heat" is due to usage of oxygen in the process of recovery; and recovery does not occur in the absence of oxygen. It is suggested that the contraction is due to liberation of lactic acid from some precursor; the acid increases the tension in some colloidal structure of the tissue; this precursor is rebuilt after contraction, oxygen is used, and heat is produced; when oxygen is absent, the heat produced is due to the breakdown of the lactic acid precursor. The oxygen appears to be used largely in oxidations whereby the molecular machine (like a steam engine charging an accumulator) builds up substances containing considerable amounts of free energy, which, as in the accumulator, can be discharged on subjecting the muscle to stimuli.   W. D. H.

The Extractives of Muscle. III. TEMISTOCLE JONA (*Zeitsch. physiol. Chem.*, 1913, **83**, 458—467).—Muscle extracts contain a fairly large percentage of gelatin, or rather of substances which behave like gelatin towards Schmidt's reagent. A dipeptide was also separated which, on analysis and determination of its constants, appears to be identical with the anhydride of *d*-alanyl-*d*-alanine, which E. Fischer prepared by treating the ethyl ester of this dipeptide with ammoniacal alcohol.   W. D. H.

Products of Protein Cleavage which Produce Fatigue, and their Influence. WOLFGANG WEICHARDT and ERWIN SCHWENK (*Zeitsch. physiol. Chem.*, 1913, **83**, 381—402).—From the muscle-

proteins, by means of electrolysis, certain high molecular products were obtained which cause, when injected into animals (mice), certain toxic symptoms, such as the signs of fatigue, slowing of the respiration, and depression of the body temperature. The effect of these *keno-toxins*, as they are termed, can be counteracted by a number of substances of which the chemical composition is known, for instance, succinimide, glutarimide, phthalimide, piperidine, creatine, guanidine hydrochloride, and others. The same effect is produced by a group of substances of unknown composition which are spoken of as *retardins*; these can be extracted by acetone from digested protein. Further work on the relationships between activity and chemical composition is promised. W. D. H.

Physiological Permeability of Cells. V. Narcosis of Lipoid-rich and Lipoid-poor Tissues of the Same Kind. LOUIS CHOQUARD (*Zeitsch. Biol.*, 1913, 60, 101—162).—Heart muscle is richer in lipoids than skeletal muscle; the effect of narcotics on each was tried in order to determine the influence of lipoids. According to the Meyer-Overton doctrine, narcotics of the aliphatic series should produce narcosis in less concentration when applied to cardiac muscle as compared to skeletal muscle. But to this a number of noteworthy exceptions were found; ether, acetone, and acetylacetone produce narcosis in smaller concentrations in the lipoid-poor skeletal than in the lipoid-rich heart muscle. Acetal narcotises heart muscle, however, in much smaller concentrations than are necessary for skeletal muscle (which is in consonance with the lipoid hypothesis), but acetal narcotises skeletal muscle in higher concentrations than ether. The introduction of a halogen atom into the molecule leads to the result that the heart muscle is narcotised by a smaller concentration than skeletal muscle. The partition coefficient, solubility in fat/solubility in water, does not account for this, for chloral hydrate, with the low coefficient of 0·22, narcotises heart muscle in the same concentration as ethyl bromide, which has a very high coefficient; probably the chemical influence of the halogenised material on the somewhat different biochemical structure of the two kinds of muscle is here being dealt with.

In the group of the univalent alcohols, the molecular weight increases as the lipoid solubility and the narcotic power in both tissues, but this relationship is not strictly parallel. For instance, the elevation of the partition coefficient of ethyl alcohol, as compared with propyl alcohol, is much greater than the rise in narcotic effect; the difference found was greater than stated by Overton.

Similar exceptional instances are found among the aldehydes. These experiments lead to the conclusion that the Meyer-Overton hypothesis is untenable. W. D. H.

The Presence of Boron in the Animal Series. GABRIEL BERTRAND and HENRI AGULHON (*Compt. rend.*, 1913, 156, 732—735). —The authors have extended their work (compare A., 1912, ii, 854) on the presence of boron in animals, and have examined twenty-

seven other species from the different classes, finding boron in practically every case. They therefore consider that boron exists normally in very small proportions in the organism of all animals, being most abundant in the species of marine origin, whilst in others it is present only to the extent of 1 part in 100,000,000 of the living matter.   W. G.

The Composition of the Tissues with Respect to Non-volatile Fatty Acids and Cholesterol, and the Possible Existence of a "Lipocytic Constant." ANDRÉ MAYER and GEORGES SCHAEFFER (*Compt. rend.*, 1913, **156**, 487—491). — The authors have determined the amount of non-volatile fatty acids and cholesterol in the various organs of a number of normal animals, and find that, whilst the variation in content of the same organ for different animals of the same species is moderately wide, more particularly in the case of the fatty acids, yet certain points stand out clearly, namely, whilst these variations occur for a given organ of animals of the same species, the values group themselves in moderate limits round a mean value, but from one species to another very different values are obtained for the content with respect to these substances for the same organ, the values being greater for birds than mammals, and still greater for eels. The so-called "lipocytic constant," $\frac{\text{cholesterol}}{\text{fatty acids}}$, is characteristic for each organ, and independent of the species.   W. G.

The Action of Ultra-violet Rays on the Ear of the Rabbit. VENCFSLAS MOYCHO (*Compt. rend.*, 1913, **156**, 577—579) —Exposure of the external surface of the ear to short irradiation (thirty seconds) produces no visible effect. If this is prolonged for one to twelve minutes, however, a series of phenomena appears. After two to five hours, local vaso-dilatation is noticeable, the portion which was exposed to the rays becoming red, this being accompanied by rise in temperature and tumefaction. The maximum effect is reached in twenty-four hours, then diminishes, and finally at the end of seven to twelve days the redness and high temperature completely disappear, and a persistent brown pigment appears. The irradiation appears to have a stimulating effect on the hair growth. The most active rays are those having $\lambda = 3100$—2900, and the cells acted on are situated at a depth of 1/10th to 1/6th mm. below the surface.   W. G.

The Influence of Heat on the Physico-chemical Behaviour of Human Milk, Cow's Milk, and Butter-Milk. PAUL GROSSER (*Biochem. Zeitsch.*, 1913, **48**, 427—432).—The milk was submitted to ultra-filtration in Bechhold's apparatus before and after boiling, and the amounts of calcium, nitrogen, and phosphorus in the filtrates were compared. It was found that after heating, the phosphorus and nitrogen in the filtrate of cow's milk was scarcely affected, whereas that of human milk was appreciably diminished.

In both kinds of milk the calcium in the filtrate diminished after heating. S. B. S.

The Therapeutic Action of Yeast on the Alimentary Multiple Polyneuritis of Guinea-pigs and Pigeons. MAX BARSICKOW (*Biochem. Zeitsch.*, 1913, **48**, 418—424).—The addition of various yeast preparations to the insufficient diet which produces the beri-beri-like symptoms in animals was investigated. In the case of guinea-pigs fed on oats and water, or on this diet with rice alone, the addition of yeast preparations exerted no beneficial effect. In the case of pigeons, however, fed on a similar diet, the beneficial effect of certain yeast preparations was marked. This effect was produced both by yeast of which the enzymes were destroyed by heat, by living yeast, and by permanent yeast preparations, but not by "cerolin," a preparation containing only the constituents of yeast soluble in organic solvents. It is suggested that the therapeutic action is due to nucleins or salts. S. B. S.

The Behaviour of Blood Sugar in Normal and Pathological Cases. VI. Blood-sugar Content in Cases of Anæmia, Liver, Intestinal and Other Diseases. FR. ROLLY and FR. OPPERMANN (*Biochem. Zeitsch.*, 1913, **48**, 471—479. Compare this vol., i, 307).—Severe anæmia, with its accompanying diseases, causes generally an increase in blood sugar, which is more or less normal in quantity in mild cases. In Greves's disease there is an increase only in severe cases. In Addison's disease the amount is either normal or subnormal; in the latter case only when the disease is severe, and unaccompanied by infectious or toxic factors (tuberculosis, etc.). In scorbutic and eclamptic cases high values are generally found, which are due partly to the toxins. An increase was also found in cases of myasthenia and gangrene. In diseases of the liver and the alimentary tract there is an increase only when toxic factors are present (carcinoma, dyspnœa, abscesses, fever, etc.). S. B. S.

The Manganese Content of Transplanted Tumours. FLORENTIN MEDIGRECEANU (*Proc. Roy. Soc.*, 1913, *B*, **86**, 174—179).—The amount of manganese in transplanted mouse and rat tumours is small (0·004 to 0·012 mg. per 100 grams of fresh material), which is about the same as in the normal mammary gland of the mouse. No differences in the manganese of sarcoma and carcinoma were discoverable. W. D. H.

The Influence of Vapours of Technical Importance on the Organism. XXXII and XXXIII. Amyl Acetate and *cyclo*-Hexanyl Acetate. KARL B. LEHMANN (*Arch. Hygiene*, 1913, **78**, 260—273).—Both the substances investigated have a relatively small toxicity, the *cyclo*hexanyl acetate being about three times as toxic as amyl acetate, as measured by the amount necessary to produce narcosis. This greater toxic effect is, however, counterbalanced by the fact that it is considerably less volatile. Both substances can be safely employed in technical operations when the necessary precautions for ventilation, etc., are taken. S. B. S.

The Influence of Certain Cardiac Medicaments on the Electrocardiam Curve. ADOLF BICKEL and MICHAEL PAVLOV (*Biochem. Zeitsch.*, 1913, **48**, 459—470).—Certain digitalis and strophanthus preparations, and especially digistrophan, have the tendency to heighten certain points in the curve, whereas, in larger doses, the height of these points is diminished. In all cases there is a lengthening both of the heart phase and pause. Cardiotonin also causes a slowing of the heart action, increasing both the heart phase and pause. Valerian has no influence in this respect. The author discusses the therapeutic application of these various drugs, as deduced from their effects on the electrocardiam curve. The experiments were carried out with dogs and rabbits.   S. B. S.

The Relationship between Heart Drugs and the Physiological Action of Cations. ARTUR VON KONSCHEGG (*Arch. expt. Path. Pharm.*, 1913, **71**, 251—260).—If a frog's heart is perfused with Ringer's solution free from calcium, the stoppage so produced can be counteracted by strophanthine; but if the solution is free from both potassium and calcium, strophanthine has not the power to resuscitate the heart. A heart poisoned with potassium again beats when strophanthine is applied. If a heart is stopped by a calcium-free solution, adrenaline and camphor cause weak contractions of the sinus, but caffeine has no effect.   W. D. H.

The Depressor Effect of Adrenaline on Arterial Pressure. WALTER B. CANNON and HENRY LYMAN (*Amer. J. Physiol.*, 1913, **31**, 376—398).—Stimulation of the cat's adrenal causes vaso-dilation and a fall of arterial pressure. Small doses of adrenaline have the same effect. After pithing, or extreme depression, the effect is pressor, but ergotoxine restores the depressor action. The effects are attributed to opposite actions of adrenaline according to the state of the muscle; relaxation occurs when the muscle is tonically shortened, and contraction when relaxed.   W. D. H.

Adrenaline and Glycamia. HENRI BIERRY and (Mlle.) LUCIE FANDARD (*Compt. rend.*, 1913, **156**, 480—482).—After injection of adrenaline to the extent of 0·001 gram per kilo. of body-weight, either intravenously or into the peritoneal cavity, there is marked progressive hyperglycamia and also a considerable rise in the combined sugar of the blood, which, however, increases more slowly than the free sugar.   W. G.

[Physiological] Action of Scopolamine. MAX CLOETTA (*Arch. expt. Path. Pharm.*, 1913, **71**, 290—292).—Polemical remarks on the controversy between Hug and Cushny (compare A., 1912, ii, 790; this vol., i, 226).   W. D. H.

The Action of Veratrine and Protoveratrine. RUDOLF BOEHM (*Arch. expt. Path. Pharm.*, 1913, **71**, 269—289).—The intensity of the action of protoveratrine on the frog's heart is much greater than that of veratrine; on nerve it is less active; on skeletal muscle

it is also less active, although its effects are substantially the same
in kind.   W. D. H.

The Behaviour in the Organism of 2-Phenylquinoline-4-
carboxylic Acid (Atophan). W. Skórczewski and J. Sohn
(*Bull. Acad. Sci. Cracow*, 1912, **9,** *A,* 885—887).—After administration
of atophan, the urine gives the following reactions: (1) A yellow
colour with concentrated hydrochloric acid. (2) A yellow precipitate
with phosphotungstic acid. (3) A dark green colour with ammonium
sulphate and ammonia. (4) A characteristic diazo-reaction with
Ehrlich's reagent. These reactions are given neither by the drug itself
nor by normal urine, but are due to an acid, which can be extracted
from the concentrated urine by ether, and which after recrys-
tallisation by ether and light petroleum has m. p. 231—232° after
turning brown at 200°. Its formula, $C_{18}H_{11}O_3N$, corresponds with
that of hydroxyphenylquinolinecarboxylic acid. The position of the
hydroxyl group in this compound is not yet determined. S. B. S.

Action of Arseno-aromatic Compounds ("606" and Neo-
salvarsan) on the Hæmoglobin of the Blood. R. Dalimier
(*Compt. rend.*, 1913, **156,** 629—631).—Salvarsan (diaminodihydroxy-
arsenobenzene) has no action on hæmoglobin either *in vitro* or *in
vivo*. Neo-salvarsan (sodium diaminodihydroxyarsenobenzene-
methylenesulphenate), on the other hand, produces marked hæmo-
lysis and reduction of the oxyhæmoglobin when acting *in vitro*. On
injection into the ear-vein of the rabbit, only a fugitive hæmolysis
is noticeable, there being no reduction of the oxyhæmoglobin.
                                                            W. G.

Chemistry of Vegetable Physiology and Agriculture.

Protein and Phosphorus Content of Azotobacter Cells.
Conrad Hoffmann (*Centr. Bakt. Par.*, 1913, ii, **36,** 474—476). Com-
pare Abstr., 1910, ii, 988).—During the course of earlier investigations
the author found the protein content of *Azotobacter* cells to vary from
8·3—12·0%, and the phosphorus content to be 2·51—2·97%. These
amounts vary considerably from those found by Stoklasa (A., 1911,
ii, 429), and it is suggested that the differences are possibly due to
differences in the methods employed in preparing the samples for
analysis. The relatively high content (61·25—71·87%) found by
Stoklasa might be attributed to removal of carbohydrates during
washing, whereas the material used by the author was obtained,
without washing, from agar cultures. If this were the case, the
protein: phosphorus ratio ought to be the same in the two sets of
results, but such agreement does not appear to exist.   H. B. H.

The Chemical Composition of Tubercle bacilli. TADEUSZ KOŹNIEWSKI (*Bull. Accad. Sci. Cracow*, 1913, **10**, *A*, 942—947).— When the bacteria are extracted with cold 96% alcohol, a small quantity of extract is obtained, which contains lipoids, colouring matter, and other substances. If the bacteria are extracted after alcohol treatment with hot acetone, relatively large quantities (20—24% of the dried bacteria) of a white, waxy substance are obtained, which is only slightly soluble on heating in most organic solvents, and is insoluble in mineral acids. On prolonged boiling with alcoholic potassium hydroxide, it yields a soap. Its formula agrees approximately with that of substance $C_{12}H_{24}O$, and the saponification number found was 125·2. The substance is probably an ester. When the bacteria are treated with 3—5% hydrochloric acid, a reducing sugar appears to pass into solution, which, even in concentrations of 2%, is optically inactive. The solution of sugar ferments with yeast. The author failed, in other experiments, to isolate glucosamine, from which he draws the conclusion that the bacteria do not contain chitin. S. B. S.

Proteus vulgaris Considered as a Producer of Indole. ALBERT BERTHELOT (*Compt. rend.*, 1913, **156**, 641—643. Compare Herter and Broeck, A., 1911, ii, 758).—Numerous observers having obtained varying results as to the production of indole by different specimens of *Proteus vulgaris*, Hauser, the author has made a careful study of the question, and finds that, in the case of the fifty-seven specimens examined, all the *Proteus vulgaris* are capable of attacking tryptophan, giving either indole or indoleacetic acid, or more generally, a mixture of these two substances, and that there is no reason for distinguishing a species *Bacillus proteus anindol·y·n·s*, as distinct from the *Proteus*-giving indole. The action of the microbe is variable not only with different specimens, but for the same race at different ages and under different conditions. W. G.

Influence of Cæsium, Rubidium, and Lithium Salts on Yeast as Compared with Potassium and Ammonium. THOMAS BOKORNY (*Bied. Zentr.*, 1913, **42**, 141—142; from *Allgem. Brauer-Hopfenzeit.*, 1912, **52**, 1469).—Addition of rubidium and cæsium sulphates to a nutritive solution containing sucrose (10), asparagine (0·1), peptone (0·025), monopotassium phosphate (0·1), and magnesium sulphate (0·025%) increased the yield of yeast, whilst lithium chloride and sulphate were injurious rather than beneficial. Potassium is essential; as much as 4·0% of monopotassium phosphate may be present without injurious effects. Ammonium salts up to 2% may be employed without injuring yeast. N. H. J. M.

Biochemical Synthesis of Alkyl Glucosides (α-Glucosides) by means of α-Glucosidase : α-Methyl Glucoside. Destruction of the α-Glucosidase in a Strongly Alcoholic Medium. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and MARC BRIDEL (*Compt. rend.*, 1913, **156**, 491—493; *J. Pharm. Chim.*, 1913, [vii], **7**, 233—236).—The authors have synthesised α-methyl glucoside by the action of

a-glucosidase, obtained from bottom yeast (compare this vol., i, 323), on a solution of dextrose in dilute methyl alcohol. The glucoside is readily hydrolysed in aqueous solution by the enzyme. Both the synthesising and the hydrolysing influence of *a*-glucosidase are destroyed by contact for forty-eight hours at 15—18° with 60% methyl alcohol. With 35% alcohol slow destruction also takes place.   W. G.

Action of Boron Compounds on the Growth of Plants. EMIL HASELHOFF (*Landw. Versuchs-Stat.*, 1913, **79–80**, 399—429. Compare Peligot, *Compt. rend.*, 1876, **83**, 686 ; Morel, A., 1892, 651 ; Loew, *Flora*, 1892. 374 ; Hotter, A., 1890, 1338 ; Nakamura, *Bull. Coll. Agric. Tokyo*, 1903. **5**, 509 ; Agulhon, A , 1910, ii, 236).—Small amounts of borax in water cultures (1 mg. per litre) acted favourably on the growth of plants, although the appearance of the plants indicated some injurious action. The same amount of boron in the form of borax diminished the yield. Both beans and maize are injured by 1·15 mg. per litre of boron.

In soil culture experiments, 0·125 mg. of boron (as borax) per kilo. of soil was not injurious to beans, whilst the same amount as boric acid is toxic. In some cases very small amounts (less than 0·1 per million of soil) seemed to have a stimulating effect.

The boron taken up by plants is deposited in the straw, and not in the seed. Although the production of spots on the leaves, under the influence of boron, seems to be the same in all kinds of plants, the effect on growth seems to vary with different plants.

                                                                    N. H. J. M.

The Value of the Chlorophyll Coefficients and their Relation to the Real Respiratory Coefficients. LÉON MAQUENNE and ÉM. DEMOUSSY (*Compt. rend.*, 1913. **156**, 506—512).—The authors have determined the respiratory quotient and the chlorophyll coefficient of some thirty-two species of plants, and as a result of this and previous work (compare A., 1912, ii, 1201) put forward a number of conclusions as to the conditions governing respiration and assimilation in the plant. In the case of green plants the normal respiratory quotient is generally greater than one during the total period of growth, but diminishes as the leaves grow older, its excessive diminution being a sign of decay or damage of the organs under observation. Leaves, with a respiratory quotient greater than one, increase the pressure of the air in which they breathe and vice versa. Certain species, particularly those rich in organic acids, are sensitive to prior conditions of light and temperature, exposure to strong light tending to diminish the respiratory quotient, but there is a particular state of equilibrium for each of such conditions, and to this, by adaptation, the plant tends to come. For a plant in equilibrium with external conditions there exists a simple relation between its apparent and real respiratory quotients and the composition of the medium in which it breathes and its coefficient of absorption for carbon dioxide, the cellular juice in a leaf sheltered from light being supersaturated with respect to the latter. The apparent chlorophyll-coefficient is generally intermedi-

ate between the respiratory quotient and unity, the real coefficient being very near to unity. Changes in the ratio hydrogen : oxygen in the composition of the vegetable tissues are due mainly, if not entirely, to respiration, and but little to assimilation. The variations of the real respiratory quotient, due to changes in temperature, arise from changes in the chemical composition of the vegetable tissues under the given conditions, the chlorophyll-coefficient being unaffected.   W. G.

Absorption of Oxygen by the Respiratory Chromogens of Plants. VLADIMIR I. PALLADIN and Z. N. TOLSTAJA (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 93—108*).—Experiments with etiolated stems of *Vicia faba* and with zymin give the following results.

The protoplasm in which the respiratory chromogens effect absorption of oxygen possesses an alkaline reaction. These chromogens may be extracted from plants by means of methyl alcohol, and, in alkaline solution, are found to absorb oxygen eagerly from the air, with formation of a cinnamon-red pigment; peroxydases or hydrogen peroxide likewise cause oxidation of the chromogens. Aqueous extracts of plants also contain chromogens able to fix atmospheric oxygen, the power to do this being weakened or completely annulled by boiling the extracts.

Chromogens extracted by means of methyl alcohol undergo scarcely any oxidation in the air, but those obtained from plants subjected for some days to autolysis in an oxygen-free medium rapidly absorb oxygen from the air with development of pigments; the addition of hydrogen peroxide prevents the formation of pigment, the liquid remaining colourless. The chromogen modified by autolysis is hence termed "reducing." Autolysis with yeast converts ordinary chromogen into the reducing modification.

Plants which, after autolysis in absence of oxygen, give a chromogen rapidly blackening in the air, give no trace of pigment when the autolysis proceeds in presence of oxygen.

The respiratory chromogen from beans is probably catechol or some derivative of it.

Alcoholic fermentation is accompanied by the formation of a substance, which readily removes hydrogen from the respiratory chromogen, and oxidises it, by means of atmospheric oxygen, to water; this withdrawal of hydrogen from the chromogen is not prevented by boiling the products of fermentation.

Thus, the respiratory chromogen, $R \cdot H_2$, like leuco-compounds, gives up its hydrogen to the absorbed oxygen with formation of pigment, R, and water.

Palladin's previous statement that, during respiration of plants the carbon is oxidised, not by the oxygen of the air, but by water, is completely confirmed by the results of Wieland's investigations (A., 1912, i, 348, 944), which showed that the oxidation of aldehydes (intermediate products of alcoholic fermentation) may proceed by removal of oxygen from water with preliminary formation of hydrates. The removal of the hydrogen formed by the decomposi-

*and *Biochem. Zeitsch.*, 1913, 49, 381—397.

tion of the water, which in Wieland's experiments was effected by means of methylene-blue or quinonoid compounds, is brought about in the case of plants by the respiratory chromogens; according to Bach, the decomposition of the water is a result of the action of reducases.

It is quite probable that, in the oxidation of chromogen to pigment, water is not immediately formed, but that the first product is either hydrogen peroxide (compare Manchot, A., 1901, i, 565, 574; ii, 93) or an organic peroxide (Bach's oxygenase).

<div align="right">T. H. P.</div>

The Migration of Mineral Constituents and the Displacement of These Constituents in Leaves Immersed in Water. GUSTAVE ANDRÉ (*Compt. rend.*, 1913, 156, 564—566).—The author has estimated the mineral constituents in the dry matter of chestnut leaves plucked at various times during the summer of 1912. The figures, whilst varying in the same direction, differ considerably from the results obtained for 1911 (compare this vol., i, 233). The total nitrogen and phosphorus diminish with increase in age of the leaf, whilst the sulphur, calcium, magnesium, and potassium increase as the leaf grows older, the increase in sulphur and calcium being probably largely due to the accumulation of calcium sulphate in the leaf.

The figures for the percentage loss of mineral matter during immersion in water for one month are of the same order as those obtained for leaves grown in 1911 (*loc. cit.*), calcium being the most resistant to exosmosis.

<div align="right">W. G.</div>

The Germination of Seeds which have been Chemically Treated and Exposed to Light. FRIEDRICH SIMON (*Biochem. Zeitsch.*, 1913, 48, 410—417).—Seeds of various plants (cress, oats, radishes) were allowed to germinate after treatment with ferric and uranyl sulphates, both when kept in the dark after the action of the reagent, and when exposed to sunlight. The percentage of the number of plants which germinated after five days was determined and compared with the number of seedlings obtained from seeds which had not been chemically treated, some of which had been exposed to light, and others kept in the dark. The results are tabulated, and it was found that in some cases (but by no means all) the seeds which had been exposed to light germinated more than those which had been kept in the dark. The action of the light and chemicals differed, however, in the different varieties of seed.

<div align="right">S. B. S.</div>

Alleged Constant Occurrence of Iodine in Cells. JOHANNA BABIY (*Ber. deut. bot. Ges.*, 1913, 31, 35—47).—The examination of numerous plants for iodine gave negative results invariably. Further experiments were made to ascertain whether plants absorb iodine from solutions containing potassium iodide. The results were negative.

The conclusion drawn by Justus (A., 1902, ii, 311) that iodine

is always present in the cell nucleus, animal and vegetable, is therefore incorrect.   N. H. J. M.

Formation of Carbamide by Higher Plants. ROBERT FOSSE (*Compt. rend..* 1913, **156**, 567—568. Compare A., 1912, ii, 1203).— Carbamide has been found in wheat, barley, maize, peas, clover, and beans, germinated under conditions excluding the presence of carbamide in the medium. Its presence has been proved in the seed during germination, but with the seed in a state of repose a negative result was obtained in the case of the white lupin and the bean, and a positive result with wheat, maize, and peas. In the case of the bean, after six weeks' germination no carbamide could be detected in the cotyledon, but it was found in the plumule to the extent of 0·112 gram per kilo. of fresh material. It was also present in the embryo of the haricot. Finally, its presence has been proved in the plumule of maize, aseptically germinated, and in the adult plant developed on a sterile, nutritive liquid according to Mazé's method.   W. G.

Presence of Callose in the Membrane of the Marine Siphonaceous Algæ [Siphonates]. ROBERT MIRANDE (*Compt. rend.*, 1913, **156**, 475—477).—The membrane of the *Caulerpa* contains no true cellulose, but is composed of two substances, one belonging to the group of pectins and the other to the calloses. This holds good for all the *Siphonates* with the exception of the *Vaucheriaceae*, which possess a celluloso-pectic membrane. The *Siphonates* thus form a distinct group, not only by reason of their anatomic characteristics, but by the chemical constitution of their membrane.
                                   W. G.

Influence of Temperature on the Development of Active Principles in Some Medicinal Plants. JAMES BURMANN (*Bull. Soc. chim.*, 1913, [iv], **13**, 246—248. Compare A., 1912, ii, 379).— By a comparison of the quantities of active principles present in colchicum, digitalis (*D. ambigua* and *D. purpurea*), aconite, and belladonna plants gathered under the same conditions each year from 1907–11 with the mean temperature prevalent during each year, the author is led to the conclusion that the alkaloidal or glucosidic content of a plant is a function of the mean temperature of the year during which it was grown.   H. W.

Production of Oxalic Acid by Aspergillus niger. CARL WEHMER (*Centr. Bakt. Par.*, 1913, ii, **37**, 31—33).—Polemical against Buromski (this vol., i, 230), with special reference to the methods used for the estimation of oxalic acid in cultures.   H. B. H.

Calotropis procera. A New Digitalis-like Drug. LOUIS LEWIN (*Arch. expt. Path. Pharm.*, 1913, **71**, 142—156).—A full botanical account is given of the plant, one of the Asclepiadeæ. The active principle is called calotropin, but it has not yet been prepared pure for chemical analysis. The main fact is expressed in the title, namely, that it belongs to the drugs which act on the heart like digitalis.   W. D. H.

Enzyme Action. IV. Occurrence of a Urease in Castor Beans. K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1913, **35**, 292—294. Compare Falk and Nelson, A., 1912, i, 523, 593; Falk and Hamlin, this vol., i, 303).—In continuation of a study of the enzymes of the castor bean, the presence of a urease has been demonstrated, which is rendered inactive by heat.   E. G.

Constituents of the Seeds of Croton tiglium. ERNST WINTER-STEIN and M. A. JEGOROV (*Landw. Versuchs-Stat.*, 1913, **79–80**, 535—539).—The seeds examined contained 5—10% of nitrogen as proteins, and 0·19 and 0·19% of nitrogen as bases and amino-acids respectively. The proteins yield the usual cleavage products. When the seeds, freed from fat, are kept for sixteen days at 37—40° in presence of toluene, chloroform, and some sodium fluoride, xanthine bases, arginine and lysine are produced. The solution from the lead acetate precipitate contained the following amounts of nitrogen: as bases, 1·437; as ammonia, 0·3514; and as amino-acids, 1·7648 grams (from 500 grams of seeds).   N. H. J. M.

The Acids of Fungi. E. HERRMANN (*Chem. Zeit.*, 1913, **37**, 206). —Oxalic, fumaric, and malic acids are widely distributed in fungi, and usually occur as calcium salts. Oxalic acid, supposed to be derived by oxidation of carbohydrate, is the commonest. Malic acid is sometimes found as potassium salt. Fatty acids also occur in fungi, particularly palmitic acid. Formic, acetic, and butyric acids are characteristic of individual species. Ergotic and sclerotic acids are characteristic of ergot. Telephoric acid, present in the cuticle of some fungi, is a pigment.   E. F. A.

Composition of Some Fungi, and the Products of Their Autolysis. ERNST WINTERSTEIN, C. REUTER, and R. KOROLEV (*Landw. Versuchs-Stat.*, 1913, **79–80**, 541—562).—The fat of *Boletus edulis* contains 0·52% of a cholesterol, m. p. 160°; $[a]_D$ −133° in 5% chloroform solution. The following substances were obtained from the fungus: inactive alanine, valine, phenylalanine, small amounts of amino-acids and trimethylamine, guanine, adenine, hypoxanthine, trimethylhistidine, and tetramethylenediamine.

In the autolysis of *Boletus*, 80—90% of the total dry matter becomes soluble; the insoluble portion contains little nitrogen. The solution contained small amounts of guanine, some hypoxanthine, but no adenine or histidine. Trimethylhistidine, much tetramethylenediamine and *iso*amylamine, and a great deal of ammonia were found.

Agaricus campestris, *Cantharellus cibarius*, and *Craterellus cornucopioides* were also subjected to autolysis.

The results show that the proteins of fungi are to a great extent decomposed into their simple crystalline cleavage products, and probably peptones and polypeptides as well. It is probable that autolytic processes occur in the symbiosis of root-nodules (compare Shibata, *Jahrb. wiss. Bot*, **37**, 643).   N. H. J. M.

The Presence of Gentiopicrin, Gentianose, and Sucrose in the Fresh Roots of Gentiana punctata. MARC BRIDEL (*Compt. rend.*, 1913, **156**, 627—629; *J. Pharm Chim.*, 1913, [vii], **7**, 289—292. Compare this vol., i, 149).—The author has isolated in a pure, crystalline state, and characterised, gentiopicrin, gentianose, and sucrose from the fresh roots of *Gentiana punctata*, and has also obtained evidence of the presence of a supposed new sugar. W. G.

Formation of Acetaldehyde during the Anaërobic Respiration of Poplar Blossom. S. KOSTYTSCHEV, ELISE HUB-BENET, and A. SCHELOUMOV (*Zeitsch. physiol. Chem.*, 1913, **83**, 105—111. Compare Palladin and Kostytschev, A., 1906, ii, 696).—Considerable quantities of freshly gathered poplar blossoms were kept in a stream of hydrogen, and the carbon dioxide, alcohol, and other volatile products formed were measured. The ratio of $CO_2 : C_2H_6O$ during respiration varied from $1.00 : 35$ to $100 : 55$, and differed from that obtained in alcoholic fermentation. In addition, acetaldehyde is formed. The amount of sugar in the fresh flowers is not large, and it is almost entirely used up during the experiment. The excess of carbon dioxide formed over that produced during alcoholic fermentation is attributed to the decomposition of other substances. The formation of acetaldehyde is considered to be due to the oxidation of active hydrogen attached to reductase and consequent partial retardation of the reduction of acetaldehyde to alcohol (compare this vol., i, 323).   E. F. A.

A New Rhubarb from Altai. ALEXANDER TSCHIRCH and M. RUSZKOVSKI (*Arch. Pharm.*, 1913, **251**, 121—136. Compare A., 1905, ii, 851; 1907, ii, 501; and Tutin and Clewer, T., 1911, **99**, 946).—A proximate analysis of roots from an unidentified species of rheum collected at Altai shows that it belongs to the "rhaponticum" group. The constituents observed are rhaponticin, chrysophanol, emodin methyl ether, emodin, dextrose, tanno-glucosides, and anthraglucosides; the last two groups of substances yield respectively rheum-red and rheonigrin on hydrolysis by acids. Rhein is absent.   T. A. H.

The Oil Seed of Ximenia Americana, L. F. SCHRODER (*Arb. Kais. Gesund*, 1912, **43**, 454—474).—An account of the constituents is given. The seeds consist of 32·3% shell, and 67·6% kernel; the latter contains 2·99% moisture, 66·0% fat, 15·2% proteins, 3·0% crude fibre, 2·19% ash, and 10·46% nitrogen free extract. No saponin, alkaloid, or cyanogenetic glucoside was found. The kernels also contain about 1% of a caoutchouc-like substance, which yields a tetrabromide. The oil varies a little in physical properties depending on the method of preparation; it is yellow, semi-solid, possesses a sharp after-taste, and has the following constants: D^{15} 0·9205 to 0·9220; saponification number, 173·2 to 177·0; iodine number, 80·3 to 85·05; Hehner number, 93·9 to 94·8; Reichert Meissl number, 1·61 to 2·45; Polenske number, 0·12 to 0·21; un-saponifiable matter, 0·46 to 0·55%. The viscosity in Engler degrees varied from 19·2 to 37·1 at 25°, and from 6·6 to 11·3 at 50°, the

highest value in each case being for oil extracted by ether, and the lowest for oil extracted by acetone. The total fatty acids included 75% of liquid fatty acids, and 10% of arachidic acid.

The shell contained 1·07% moisture, 5·9% fat, 9·05% proteins, 24·83% crude fibre, 12·78% ash, and 46·32% nitrogen-free extract.

T. A. H.

Biochemistry of Sea Weeds. HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1913, **83**, 171—197).—Fucosan, the constituent of the bladders of the *Fucoideæ* which is coloured red by vanillin and hydrochloric acid, has strong reducing properties; it is precipitated by lead acetate and in acid solution by gelatin solutions. Its solutions have an adstringent taste resembling tannin. On oxidation, phycophæin is obtained. No sugar is eliminated on boiling fucosan with dilute sulphuric acid.

Mannitol has been found in several *Fucus* and *Laminaria* species The sweet-tasting, white substance, which often covers the whole thallus of *Laminaria* on drying, is mannitol.

Dextrose or lævulose were found in small quantity in four of the *Fucoideæ* investigated, but in none of the *Florideæ*. Several of the *Fucoid-æ* contain also a dextrin-like polysaccharide, laminarin, which is regarded as a reserve material built up from dextrose and corresponding with starch in the higher plants.

Two species, *Ascophyllum nodosum* and *Fucus vesiculosus*, which contain fat, contained very little laminarin.

The *Florideæ* contain starch, which gives dextrose when boiled with dilute acids, and is quickly hydrolysed by malt diastase.

The seaweeds are rich in slimy cell-wall constituents. Algin and fucidin, obtained from the *Fucoideæ*, are described briefly, as well as similar products from the *Florideæ*.   E. F. A.

Nutrition of Green Plants with Ammonium Salts. ENRICO PANTANELLI and G. SEVERINI (*Bied. Zentr.*, 1913, **42**, 98; from *Staz. sper. agrar. ital.*, 1911, **44**, 873).—Sand-culture experiments in which wheat and mustard were supplied with different ammonium salts under sterilised conditions. Sodium nitrate was also employed.

The greatest amounts of leaf were obtained with sodium nitrate, whilst ammonium salts produced the greatest amount of seed.

The only injurious effects were observed when ammonium chloride was employed, and in the case of mustard, with ammonium citrate. The best results with wheat were obtained with the organic ammonium salts, then the insoluble ammonium magnesium phosphate, and next with sodium nitrate. Mustard developed most quickly under the influence of sodium nitrate.   N. H. J. M.

Changes of Phosphoric Acid in Plants at Different Periods of Growth and with Different Phosphorus Manures. LEOPOLD SEIDLER (*Landw. Versuchs-Stat.*, 1913, **79—80**, 563—610).—Pot experiments in which barley and oats were grown in different soils, without phosphorus and with superphosphate, bone meal, and basic slag respectively.

The result obtained by Staniszkis with millet, indicating that the nitrogen increases in the parts above ground to the end, was partly confirmed. In the roots, however, there is a diminution in the amount of nitrogen. The amount of phosphoric acid taken up is not always in proportion to the production of dry matter. Inorganic phosphates which, at first, are taken up in considerable amounts are, as vegetation proceeds, to a great extent converted into organic phosphorus compounds. In barley the organic phosphorus is chiefly in the forms of protein and lecithins, whilst in oats phytin frequently predominates. The phosphoric acid of phytin, which generally forms only a fraction of the total phosphoric acid, increases in the whole plant to the end of the vegetative period; in the roots it generally diminishes.

As regards the relation between the inorganic and organic phosphorus, the latter increases in barley, and generally in oats, as vegetation proceeds; in oats, however, the amount of organic phosphorus generally remains less than the inorganic phosphorus.

N. H. J. M.

The Significance of the Lime–Magnesia Ratio in Soil Analyses. P. L. GILE and O. N. AGETON (*J. Ind. Eng. Chem.*, 1913, **5**, 33—35).—Loew has put forward the hypothesis that plants make their maximum growth, other factors being favourable, only when the available lime and magnesia are present in a ratio which may vary from 1:1 to 4:1. The authors have made observations on Porto Rican soils, and obtained very conflicting results, finding that soils with lime-magnesia ratios varying from 30:1 to 500:1 are productive pineapple soils; that one soil with the ratio 25:1 is an exceptionally productive soil for citrus fruits and pineapples; that another soil, where the ratio varies from 22:1 to 1461:1 is an exceptionally productive soil for sugar cane.

It may be that the apparently confirmatory results arrived at by some investigators are to be attributed rather to alterations in the soil reaction than to the lime-magnesia ratio. It would appear that in analyses of ordinary soils the above ratio is of no significance, but in analyses of the soluble salts of alkali soils the ratio may be exceedingly important. T. S. P.

Weathering of Soil. G. H. LEOPOLD (*Chem. Weekblad*, 1913, **10**, 70—86).—An investigation of the conditions affecting the formation of various types of soil by weathering, based on a large number of analyses of dark grey and red loams. A. J. W.

Two Volcanogenic Loams from Japan. TOYOTARO SEKI (*Landw. Versuchs-Stat.*, 1913, **79-80**, 871—890).—Analyses of two loams from Tokio and from North-East Japan. The soils possess only a slight plasticity when kneaded with water, and are friable when dry. The soils do not contain zeolites, and their deficient plasticity is attributed to the absence of aluminium hydroxides and to the presence of allophanoids. N. H. J. M.

Organic Chemistry.

Some Data of the Solubility of Metallic Copper in the Different Fractions Obtained by the Distillation of Crude Petroleum. CONSTANTIN I. ISTRATI and C. TEODORESCU (*Bull. Acad. Sci. Roumaine*, 1912/3, **1**, 19—25).—The requisite petroleum was obtained by fractionating crude petroleum taken from the Moreni reservoir. Eight fractions were collected, the extreme values of the b. p. being 100° and 300° respectively, each fraction having a range of b. p. of 25°. The separate fractions were placed in sunlight after addition of an excess of purely divided metallic copper. In general, the amount of copper salt formed increased with increasing b. p. of the fraction, the values observed varying from 0·022 gram per 100 c.c. for fraction b. p. 100—125° to 3·499 grams per 100 c.c. for fraction b. p. 275—300°. A notable exception to this regularity occurs with the portion of b. p. 250—275°, which dissolves less copper than either the preceding or succeeding fraction. Determination of the acidity of these fractions, whether by extraction with alcohol or by direct estimation with alcoholic potassium hydroxide, shows that this factor increases regularly with increasing b. p. of the fractions. The authors are led to the conclusion that this apparent anomaly is due to the presence of a larger proportion of lactones in the fraction b. p. 250—275°, which, although capable of neutralising alkali, are unable to attack metallic copper. This view is confirmed by the fact that a greater quantity of lactones can be extracted by means of alcohol from the fraction b. p. 250—275°, which has been treated with metallic copper, than from a similarly treated fraction, b. p. 225—250°.　　　　H. W

The Composition of Illuminating Gas. PAUL LEBEAU and A. DAMIENS (*Compt. rend.*, 1913, **156**, 797—799).—Combining the ordinary methods of gas analysis with their own methods for analysing mixtures of gaseous hydrocarbons (this vol., ii, 253), the authors have made very complete analyses of three different samples of illuminating gas, and their results, which are tabulated, establish the presence of higher homologues of methane. Their values for carbon monoxide are somewhat lower than the generally accepted figure for that constituent.　　　　W. G.

Mechanism of the Transformation of Stereoisomeric Ethylene Compounds. RICHARD STOERMER (*Chem. Zentr.*, 1913, i, 693—694; from *Sitzungsber. Abh. Naturforsch. Ges. Rostock*, 1912, **4**, 35—43).—The transformation of stable ethylene compounds into labile stereoisomerides by means of ultraviolet light (A., 1911, i, 295) cannot be explained by the theories of Wislicenus, Nef, or Aschan. Only Werner's conception of the carbon atom offers any assistance, and this has now been developed so as to include *cis-trans*-isomerism in ring compounds.　　　　J. C. W.

Elimination of Water from Pinacolyl Alcohol and on Tertiary Butylethylene. W. FOMIN and N. SOCHANSKI (*Ber.*, 1913, **46**, 1219. Compare this vol., i, 331).—The hexylene which Delacre obtained by the action of sodium on the chloride, $CMe_3 \cdot CCl{:}CH_2$ (A., 1906, i, 476), was also *tert.*-butylethylene ($\gamma\gamma$-dimethyl-Δ^β-butylene). The hydrocarbon, "pseudo-butylethylene," b. p. 56—58°, which accompanied the $\beta\gamma$-dimethyl-Δ^β-butylene (Couturier, A., 1893, i, 244) had in the meantime been identified as $\beta\gamma$-dimethyl-Δ^α-butylene.   J. C. W.

Preparation of $\beta\gamma$-Dimethyl-$\Delta^{\alpha\gamma}$-butadiene. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 256717).—It is found that the yield of $\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene obtained from pinacone or pinacolin (A., 1911, i, 829) can be increased to 80% if the operation is carried out at 450° and under reduced pressure.   F. M. G. M.

Preparation of Diolefines. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 255519).—When monohalogenated olefines, dihalogenated paraffins or halogenated alcohols are heated at 300—500° at ordinary or reduced pressures with catalytic agents, such as barium chloride, nickel chloride, lead chloride or aluminium hydroxide, they furnish satisfactory yields of the corresponding diolefines, and the preparation of isoprene by this method from the following substances is now recorded.

From (1) $\beta\gamma$-dibromo*iso*pentane, $CMe_2Br \cdot CHBrMe$, (2) $\beta\gamma$-dichloro*iso*-pentane, (3) $\alpha\gamma$-dibromo*iso*pentane, $CMe_2Br \cdot CH_2 \cdot CH_2Br$, (4) $\alpha\beta$-dibromo-*iso*pentane, $CHMe_2 \cdot CHBr \cdot CH_2Br$, (5) γ-bromo-β-methyl-Δ^β-butylene, $CMe_2{:}CMeBr$, (6) β-chloro-β-methylbutan-γ-ol, $CMe_2Cl \cdot CHMe \cdot OH$, (7) from the acetate of γ-bromo-β-methylbutan-α-ol,
$$OAc \cdot CH_2 \cdot CHMe \cdot CHBrMe,$$
whilst $\beta\gamma$-dibromobutane, $CHMeBr \cdot CHBrMe$, furnishes divinyl, hexylene dibromide gives rise to hexadiene, b. p. 68—77°, and dichloro-*n*-pentane yields $\Delta^{\alpha\gamma}$-pentadiene, b. p. 38—45°.   F. M. G. M.
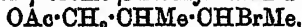
The Action of Monosodioacetylene on the Alkyl Iodides. Preparation of True Acetylenic Hydrocarbons. PAUL LEBEAU and MARIUS PICON (*Compt. rend.*, 1913, **156**, 1077—1079).—Mono-sodioacetylene, prepared by the action of acetylene on sodium dissolved in liquid ammonia, when dissolved in the same solvent readily reacts with the alkyl iodides, giving the corresponding acetylene hydrocarbons, in nearly theoretical yield. The ammonia is removed by absorption with water, the last traces being eliminated by dilute sulphuric acid. By this method the authors have prepared allylene and hexinene.
                                                    W. G.

Preparation of Primary Alcohols by Reduction of the Esters with Absolute Alcohol and Sodium-ammonia. E. CHABLAY (*Compt. rend.*, 1913, **156**, 1020—1022).—Sodium in liquid ammonia reacts with esters of monobasic acids according to the equation : $3R \cdot CO_2R' + 4NH_3Na = 2R \cdot CONH_2 + R \cdot CH_2 \cdot ONa + 3R' \cdot ONa + 2NH_3$ (compare A., 1912, i, 244). Coupling this with the action of absolute alcohol on the sodium, giving nascent hydrogen, the

amide in its turn is converted into the corresponding primary alcohol, the whole of the acid being thus reduced to primary alcohol:
$$2R \cdot CO \cdot NH_2 + 4H_2 = 2R \cdot CH_2 \cdot OH + 2NH_3.$$
The ester dissolved in absolute alcohol is poured on to the solution of sodium in ammonia at $-80°$. When the action is complete, the residue is decomposed by water, distilled in steam, and the mixture of alcohols separated by fractionation. The corresponding alcohols have thus been prepared from the esters of a number of the higher fatty acids. The esters of dibasic acids are similarly reduced, giving dihydroxy-alcohols; methyl sebacate gives decane-$\alpha\kappa$-diol, m. p. $71 \cdot 5°$. Ethyl phenylacetate gives phenylethyl alcohol, whilst methyl cinnamate gives, not cinnamyl alcohol, but the saturated phenylpropyl alcohol.   W. G.

New Methods of Spirit Rectification. HUGO MASING (*Chem. Zeit.*, 1913, **37**, 329—330).—It has hitherto been usual to dilute the raw spirit with water before submitting it to the process of rectification. It has been found in Russia, however, that better results are obtained when the undiluted spirit is used. In order to find out the reason, the author has constructed a special still-head, a modification of the Le Bel and Henninger form, in which there are taps to the side-tubes so that the liquid flowing from any one of the bulbs can be collected for analysis.

The results show that the strength of the spirit collecting in the bulbs increases more slowly than according to Gröhning's tables (compare A., 1908, i, 751), the slowest rate of increase being with the very dilute spirit. The Russian method of rectification is therefore justified.   T. S. P.

$\beta\gamma$-Dimethylbutan-α-ol. ALEXANDER I. GORSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 167—169).—Ethyl $\alpha\beta$-dimethylbutyrate, $C_8H_{16}O_2$, has b. p. 148—$150°/745$ mm., $D_4^{17} \; 0 \cdot 8719$, $D_4^{27 \cdot 3} \; 0 \cdot 8647$, $n_D^{18} \; 1 \cdot 4048$.

$\beta\gamma$-Dimethylbutan-α-ol, $C_6H_{14}O$, obtained by reducing the above ester by means of sodium in alcoholic solution, is a viscous liquid, b. p. 144—$145°/761$ mm., $D_4^{20 \cdot 5} \; 0 \cdot 8297$, $n_D^{20 \cdot 5} \; 1 \cdot 4195$, and forms a urethane, $C_{18}H_{19}O_2N$, m. p. 28—$29°$.   T. H. P.

New Data Concerning the Oxide of Pentamethylene Glycol. NICOLAI J. DEMJANOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 169—173).—Since the action of nitric acid on pentamethylene-diamine gives, in addition to pentamethylene glycol, a small proportion of an isomeric glycol, it is probable that the oxide obtained by the author (A., 1892, 1292) by heating pentamethylenediamine nitrite and by the action of sulphuric acid on the glycol prepared from pentamethylenediamine, and also that obtained by Hochstetter (A., 1903, i, 305) by the action of water on the bromide corresponding with the glycol from pentamethylenediamine, are not chemical individuals. Further, it is possible that the action of sulphuric acid on pure pentamethylene glycol may be accompanied by isomeric change, with formation of the oxide, $O{<}^{CHMe \cdot CH_2}_{CH_2-CH_2}$.

The author has therefore prepared the pure oxide by heating penta-methylene bromide in a sealed tube. This oxide, $C_7H_{10}O$, is a liquid, b. p. 86·5—87·5°/743 mm., D_0^{15} 0·883, D_0^0 0·900, n_D^{15} 1·4195, and on oxidation with nitric acid yields mainly succinic acid, its structure being thus confirmed. These properties agree closely with those given by Harries (A., 1911, i, 798) for his 3-methyltetrahydrofuran, and it may be that in the formation of this compound by the reduction of ethyl pyrotartrate, isomeric change occurs.   T. H. P.

Development of Heat on Mixing Ether and Chloroform. (Mme.) MARCELET and H. MARCELET (*Chem. Zentr.*, 1913, i, 229; from *Bull. Sci. Pharmacol.*, 1912, 19, 676—677).—Heat is developed when ether and chloroform are mixed, the maximum effect resulting from equal volumes; 25 c.c. of each liquid give a rise in temperature from 16·6° to 30·3°.   J. C. W.

The Constitution of Sulphurous Acid. WILHELM STRECKER (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913, 126).—In continuation of previous investigations (A., 1910, i, 532), the sulphoxides have been prepared from symmetrical diethyl sulphite, and investigated optically. No details are given, but the conclusion arrived at from the optical results is, that there is no change in valency of the sulphur when a sulphoxide is oxidised into the sulphone; this is not in accordance with the chemical behaviour of these compounds.   T. S. P.

Decomposition of Formates. WILLIAM ŒCHSNER DE CONINCK and ALBERT RAYNAUD (*Rev. Gen. Chim. pure appl.*, 1912, 15, 455—456).—When sodium formate is heated, a complex mixture of substances is evolved containing aqueous vapour, aldehydes (among which acraldehyde has been identified, A., 1912, i, 527), oily substances, formic acid, and small quantities of carbon dioxide. The residue contains sodium carbonate, sodium hydroxide, and carbon.

Sodium, calcium, barium, potassium, and lead formates are decomposed to a greater or less extent when treated with pure methyl alcohol at its b. p. Formic acid was detected by distilling a portion of the alcohol and testing with silver nitrate solution after addition of water. When ethyl alcohol is substituted for methyl alcohol, very little decomposition is observed in the cases of sodium and calcium formates, whilst barium, potassium, and lead formates are rather more sensitive to the decomposing action of this reagent.

Solutions of lead formate, when exposed to diffused light during four months, are partly decomposed with the liberation of formic acid. Under similar conditions, uranium formate is completely decomposed in methyl-alcoholic solution within three months (compare this vol., i, 333).   H. W.

Catalytic Esterification in Dilute Solutions: Preparation of Ethyl Acetate. FERNAND BODROUX (*Compt. rend.*, 1913, 156, 1079—1081. Compare Senderens and Aboulenc, A., 1911, i, 600, 637; ii, 1080; 1912, i, 694).—By distilling mixtures of ethyl alcohol and acetic acid diluted with water containing varying quantities of sulphuric

acid, ethyl acetate is obtained, the yield of the ester from given quantities of alcohol and acid varying with the amount of sulphuric acid in the water. With 10% sulphuric acid, a yield of 92% of ethyl acetate is obtained. The sulphuric acid can be replaced by numerous other acids as catalysts, but they are less effective. W. G.

The Hydrolysis of Fats. JULIUS MARCUSSON (*Zeitsch. angew. Chem.*, 1913, **26**, 173—176).—It is now generally accepted that the hydrolysis of fats in a homogeneous system takes place in steps with intermediate formation of diglycerides and monoglycerides (Fortini, A., 1912, i, 826; Grün and Corelli, A., 1912, i, 409; Fanto and Stritar, A., 1908, i, 499, and others). The present state of knowledge of the process of hydrolysis in a heterogeneous system, for example, by alkali, is not so satisfactory (compare Marcusson, A., 1906, i, 924; 1907, i, 674). Kellner (A., 1909, i, 357, 548, 759) obtained indications of a graded hydrolysis by superheated steam, but unfortunately used natural palm-kernel oil, which, as a mixture of triglycerides, might give misleading results. The author has investigated the hydrolysis of simple triglycerides, such as tribenzoin, tristearin, and tripalmitin, by heating with water in an autoclave; after this treatment the triglyceride had a. m. p. several degrees lower, and in the case of the two latter fats, treatment with acetic anhydride (during which "aceto-lysis" did not occur; Willstätter and Madinaveitia, A., 1912, ii, 1104) gave a product which showed a considerably higher saponification number than the original triglyceride. Palm-kernel oil exhibited similar behaviour. From these results it appears that the hydrolysis of fats by water, and therefore presumably also by acids and enzymes, is a bimolecular process.

The author favours the view that the exceptional behaviour of alkali, which appears to hydrolyse directly to glycerol, is due to hydrolysis occurring mainly at the contact surface of fat and aqueous liquid; on account of the slow rate of diffusion of the intermediate diglycerides and monoglycerides, and the relatively great rapidity of their hydrolysis, no appreciable quantity of these substances can escape into the main body of fat again. In the above autoclave experiments, however, the elevated temperature increases the velocity of diffusion of the substances, whilst the hydrolysis is relatively much slower, so that the escape of the intermediate products from immediate further hydrolysis is facilitated. D. F. T.

Glycerides of Fats and Oils. IV. The Mixed Glycerides of Palmitic and Stearic Acids Obtained from Lard. ALOIS BÖMER (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 321—353. Compare A., 1912, i, 600).—By repeated fractionation from ether, pure glycerides of saturated fatty acids were isolated from lard; the least soluble glyceride so obtained was found to be a palmityldistearin, and not heptadecyldistearin as stated by Kreis and Hafner. Tristearin is not present in lard. The palmityldistearin separated from lard had m. p. 68·5° (corr.), and differed in this respect and also in its crystalline form from the similar glyceride separated from mutton fat; the former is probably α-palmityldistearin, whilst that from mutton fat is β-palmityl-

distearin. The lard under examination contained about 3% of a-palmityldistearin, and about 2% of another saturated glyceride, namely, stearyldipalmitin, m. p. 58·2° (corr.).   W. P. S.

Glycerides of Fats and Oils. V. Nomenclature of Mixed Glycerides and the Synthesis of α Distearin and β-Palmityldistearin. ALOIS BÖMER and R. LIMPRICH (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 354—366).—It is suggested that, in the case of mixed glycerides, where different fatty acid radicles are combined with the same glycerol molecule, the position of the fatty acid radicles should be denoted by the letters α, β, and γ respectively. In the preparation of α-distearin from α-dichlorohydrin and potassium stearate (compare A., 1903, i, 788) considerable quantities of tristearin are also formed ; again, tristearin and possibly stearyldipalmitin are produced together with β-palmityl-distearin when the latter is prepared from α-distearin and palmitic acid. α-Distearin has m. p. 78·5° (corr.), and β-palmityldistearin has m. p. about 63°, and is identical with the palmityldistearin separated from mutton fat.   W. P. S.

China Oil. SERGEI A. FOKIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 283—285).—The polymerisation of this oil when heated, the increased refraction, and the transformation of the elæomargaric acid under the influence of light into a product with a higher melting point are explainable on the assumption that the acid contains either conjugated double linkings or, as in allene, a carbon atom with two double linkings. The products obtained when the acid is oxidised with alkaline permanganate solution indicate its structure to be :

$$CH_3 \cdot [CH_2]_3 \cdot CH:CH \cdot CH:CH \cdot [CH_2]_9 \cdot CO_2H.$$ T. H. P.
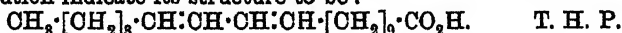
Behaviour of Certain Unsaturated Acids Towards Selenious Acids. SERGEI A. FOKIN (*J. Russ. Phys. Chem. Soc*, 1913, **45**, 285—286).—Various unsaturated aliphatic acids and, more especially, the oils containing them as glycerides, undergo marked changes when heated with concentrated solutions of selenious acid at 100° under the ordinary pressure. This action is most characteristic in the case of castor oil. After one to three hours' heating, the oil becomes converted into a caoutchouc-like mass of a faint red colour. This product is insoluble in alcohol, ether, benzene, pyridine, etc., but it dissolves with decomposition in boiling acetic acid, and is saponified and darkened by alcoholic potassium hydroxide. When treated with alcohol or ether, it swells to a jelly, which can be readily pounded to a paste and, after evaporation of the alcohol or ether in the cold, reduced to powder. After being washed to remove any excess of selenious acid or castor oil, the powder has the iodine number 59·0 and the saponification number 168·5, the corresponding numbers for castor oil being 86 and 180 respectively. The substance contains selenium, and the presence of double linkings and the small difference between its saponification number and that of the original oil indicate it to be different from the "factis" obtained by the action of sulphur di- or tetra-chloride on linseed and other oils.   T. H. P.

Formation, Decomposition, and Transformation of Glycollic Acid. EMIL BAUR (*Ber.*, 1913, **46**, 852—863).—It is found that the reduction of oxalic acid to glycollic acid which can be effected by electrolytic reduction with lead, or less well with platinum, cathodes (A., 1908, i, 600), also occurs to some extent when a solution of oxalic acid with formic acid is submitted to the action of finely divided rhodium (Schade, A., 1908, i, 136; Blackadder, this vol., ii, 36) or of platinised platinum foil. The metal causes the decomposition of the formic acid into hydrogen and carbon dioxide, the former of which effects a reduction of the oxalic acid through glyoxylic acid to glycollic acid. Small quantities of the two last substances can be detected in the final mixture.

In the presence of coloured metallic salts, glycollic acid is affected by exposure to the light of a quartz mercury lamp, being partly converted into formaldehyde and formic acid. The following salts, copper sulphate, uranic and uranous sulphates, and ferric sulphate all exerted this effect, but the first-named was least active and the last-named most.

When tubes of quartz glass containing an aqueous solution of calcium glycollate or of a mixture of calcium glycollate and calcium malate are submitted to the light of a quartz-mercury lamp for one hundred and forty hours, a certain amount of calcium citrate is formed (compare Ciamician and Silber, A., 1911, i, 513, 650); the same condensation to citric acid occurs when saturated solutions of calcium glycollate or calcium malate, mixed with one and a-half times their bulk of saturated lime-water, are kept for a few days. Although it was not possible to prove the presence of a malate in the solution of calcium glycollate after exposure to light, the accidental growth of a mould in a solution of calcium glycollate caused the formation of minute crystals of calcium malate.

In connexion with his view that oxalic acid is the first product of assimilation of carbon dioxide in plants (A., 1908, ii, 780), the author draws attention to the manner in which the above results render oxalic acid a possible origin of the common vegetable acids; further, by its scission into formaldehyde and formic acid, glycollic acid may possibly be the source of the sugars. D. F. T.

Method of Preparing Ethyl γ-Chloroacetoacetate. DIMITRI K. ALEXANDROV (*Ber.*, 1913, **46**, 1021—1024).—By the interaction of magnesium powder with ethyl α-chloroacetate, a condensation product of two molecules, $CH_2Cl\cdot C(OEt)(O\cdot MgCl)\cdot CH_2\cdot CO_2Et$, is formed, which is decomposed by water into ethyl γ-chloroacetoacetate. This is a colourless oil, b. p. 107°/14 mm., giving a red coloration with ferric chloride, D_4^{20} 1·2157, n_D^{17} 1·4546. The copper salt crystallises in thin, matted, pale green needles, m. p. 168—169° (decomp.). E. F. A.

Action of Oxalyl Chloride on Several Organic Derivatives. HERMAN J. TAVERNE (*Chem. Weekblad*, 1913, **10**, 214—223. Compare Graebe and Liebermann, *Ber.*, 1869, **2**, 678; Staudinger, A., 1908, i, 938; 1909, i, 796, 905; 1912, i, 567; Jones and Tasker, T., 1909, **95**, 1904; Liebermann and Zsuffa, A., 1911, i, 202;

Liebermann, A., 1911. i, 656; 1912, i, 464; Bornwater, A., 1911, i, 616).—A summary of work on the reactions of oxalyl chloride previously published.   A. J. W.

Solubility of Thorium Oxalate. A. COLANI (*Compt. rend.*, 1913, **156**, 1075—1076. Compare Wirth and Hauser, A, 1912, i, 827).—A study of the solubility of thorium oxalate, alone or in the presence of oxalic acid, in hydrochloric acid at 17° and 50°. For varying concentrations of hydrochloric acid. the amount of oxalate dissolved is independent of the amount in contact with the liquid. With moderately strong acid, the oxalate is converted into chloro-oxalate with the elimination of oxalic acid, which consequently diminishes the solubility of the chloro-oxalate. The solubility of the thorium oxalate in hydrochloric acid is greatly diminished by the presence of small amounts of oxalic acid.   W. G.

Preparation and Properties of the Ammonium Salts of Some Organic Acids. LeRoy McMaster (*Amer. Chem. J.*, 1913, **49**, 294—301).—Keiser and McMaster (this vol., i, 248) have described a method for the preparation of normal ammonium salts of dibasic organic acids. In continuation of this work, ammonium *malonate,* succinate, *malate, tartrate,* phthalate, and iso*phthalate* have been prepared. The method has also been used for obtaining the salts of certain monobasic acids, and ammonium *propionate,* iso*butyrate, palmitate, benzoate,* and *cinnamate* are described.   E. G.

Crystalline Form and Optical Properties of Magnesium Malate. O. I. MOROSCHKINA (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 225—230).—Magnesium malate, $MgC_4H_4O_5 5H_2O$, crystallises in hemihedral forms of the rhombic system: $a:b:c = 0.7476:1:0.4096$ (compare Traube, A., 1899, i, 484). The etched figures and optical properties are described.   T. H. P.

Tetrolaldehyde (Δ^a-Butinal) and Some of Its Derivatives. PAUL L VIGUIER (*Ann. Chim. Phys.*, 1913, [viii], **28**, 433—536).—A résumé of the work accomplished, and already abstracted, on this subject since 1908.   T. A. H.

Catalytic Hydrogenation of Acetone. A. LASSIEUR (*Compt. rend.*, 1913, **156**, 795—797. Compare Haller and Lassieur, A., 1910, i, 355).—The hydrogenation of acetone by the method of Sabatier and Senderens at temperatures above 200° yields neither iso*propyl* alcohol nor a pinacone, but the principal product is methyl iso*butyl* ketone, together with a small quantity of valerone and some still more highly condensed products.   W. G.

Migration of the Chlorine in the Halogenated Ketones. EDMOND E. BLAISE (*Compt. rend.*, 1913, **156**, 793—795. Compare this vol., i, 11).—By the chlorination of methyl ethyl ketone in the presence of water and marble a mixture of three chlorinated ketones is obtained. The smallest fraction is dichloromethyl ethyl ketone, b. p. 31°/

33—34 mm. The second and largest fraction is chloromethyl α-chloro-ethyl ketone, b. p. 165° (compare Vladesco, A., 1892, 424). The third constituent is methyl α-dichloroethyl ketone (compare Favorski and Desbout, A., 1895, 497). On heating dichloromethyl ethyl ketone with a mixture of hydrochloric and acetic acids on a water-bath for six hours, 50% of it is conveited into chloromethyl α-chloroethyl ketone, one of the chlorine atoms having migrated. Increase in the amount of hydrochloric acid in the mixture facilitates the migration. W. G.

Reduction of Acetobromoglucose and Similar Substances. EMIL FISCHER and KARL ZACH (*Sitzungsber. K. Akad. Wiss. Berlin.* 1913, 311—317).—On reduction of acetobromoglucose by means of zinc dust and acetic acid at the ordinary temperature, a crystalline compound, $C_{12}H_{16}O_7$, is obtained, together with a molecule of acetic acid. The new compound, *acetoglucal*, takes up two atoms of bromine. On hydrolysis three molecules of acetic acid are eliminated, and *glucal*, $C_6H_8O_3$, a soluble viscid syrup, b. p. 170—185°/0·2 mm. pressure, is obtained. This behaves as an aldehyde, and forms oily hydrazones, but no osazones. It decolorises bromine in aqueous solution, and is decomposed by acids, giving an intense green pine-splinter reaction when heated with hydrochloric acid.

Provisionally the formula $\begin{matrix} CH \cdot CH(CH_2 \cdot OH) \\ CH \text{——} CH(CHO) \end{matrix} {>}O$ is suggested.

Acetobromogalactose and acetobromolactose behave similarly when reduced, but only oily products were obtained.

Acetoglucal has m. p. 54—55°, $[\alpha]_D^{20} - 13 \cdot 02°$. E. F. A.

Phytin. R. H. ADERS PLIMMER and HAROLD J. PAGE (*Biochem. J.,* 1913, **7,** 157—174).—Inorganic phosphates in phytin can be estimated by precipitation with ammonium molybdate in semi-normal nitric acid at room temperature. The calcium can be estimated by precipitation as calcium sulphate, but not as oxalate. The magnesium can then be estimated as pyrophosphate. There is great difficulty in removing the calcium from phytin in the preparation of phytic acid. The yield of inositol on hydrolysis of the latter is not quantitative; there is possibly another organic constituent in phytin. W. D. H.

Transformation of *l*-Arabinose into *l*-Ribose. WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad,* 1913, **10,** 213—214).—Heating with dilute aqueous sodium hydroxide partly converts *l*-arabinose into *l*-ribose, the presence of the latter in the mixture being proved by oxidising the two pentoses to arabonic acid and ribonic acid, converting these acids into their phenylhydrazides, and separating the hydrazides by fractional crystallisation.

A. J. W.

Action of Hydrogen Peroxide and Ferric Chloride on Starch. O. DUBIEUX (*Bull. Soc. chim. Belg.,* 1913, **27,** 90—97. Compare Neuberg and Miura, A., 1911, i, 935; Gerber, A., 1912, i, 538).—Hydrogen peroxide solution does not hydrolyse soluble starch prepared by Fernbach's method at the ordinary temperature, and the

same is true of colloidal solutions of iron or of mixtures of these two products. Similarly, a solution of ferric chloride does not hydrolyse starch, but when used along with hydrogen peroxide it causes hydrolysis at an appreciable rate, which increases with the quantity of ferric chloride employed. The results of experiments designed to test the influence of various factors on the reaction show that the quantity of reducing substances formed depends on the quantity of peroxide used, and that the acidity of the mixture increases with the quantity of reducing substances formed. The hydrogen peroxide is decomposed, but no oxygen is evolved unless the peroxide is present in excess. The iron remains in the ferric state until hydrolysis is complete, when it suffers reduction, the reducing substances disappearing at the same time. Measurements of the rate of hydrolysis show that the reaction does not follow the logarithmic law for a unimolecular reaction. Hydrogen peroxide reduces the rate of hydrolysis of starch by diastase and does not undergo decomposition itself.   T. A. H.

Starch of Glutinous Rice and Its Hydrolysis by Diastase. Yoshio Tanaka·(*J. Ind. Eng. Chem.*, 1912, 4, 578—581).—The starch of glutinous rice is characterised by giving a red coloration with iodine ; the microscopic characteristics of these starch granules and the hydrolysed products do not apparently differ in any way from those of common rice starch. The starch of glutinous rice does not contain amylodextrin, erythrodextrin, or the special proteins which have previously been considered to be the cause of the red iodine coloration ; nor does it contain any of the common starch, which gives a blue colour with iodine.

Glutinous rice starch is, moreover, rapidly hydrolysed by diastase to dextrin with the production of a less amount of maltose than in the case of equal quantities of potato or common rice starch ; the author considers that glutinous rice starch contains a larger amount of amylopectin, or some analogous constituent which produces a dextrin that hydrolyses more slowly with diastase than does that from ordinary starch.

It is probable that there are many other cereals in Nature containing a similar variety of starch, its presence having been noted in glutinous millet, glutinous *Panicum miliaceum*, L., and in *Andropogon Sorghum*. The separation of glutinous from common rice starch is comparatively simple, as the former is opaque, the latter translucent.
F. M. G. M.

The Acetolysis of Cellulose to Dextrose Acetate. Hermann Ost (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1913, 124—125).—The end-product of the acetylation of cellulose is cellobiose octa-acetate (compare A., 1912, i, 680), which is readily obtained in a pure crystalline condition when a mixture of 5 grams of cellulose with 25 c.c. of acetic anhydride and 2·5 grams of concentrated sulphuric acid is kept at the room temperature for some days, or even weeks ; the yield is 33%. The reaction proceeds farther on warming. For example, a mixture of 5 grams of cellulose, 25 c.c. of acetic anhydride, 25 c.c. of glacial acetic acid, and 5 grams of concentrated sulphuric acid when heated

for three days at 45° no longer gives cellobiose octa-acetate ; by extraction with ether, a syrup consisting of a mixture of dextrose penta-, tetra-, and tri-acetates is obtained, which by further acetylation can be transformed into dextrose α-penta-acetate, m. p. 112°, and a rotation of +101·7°. The same product can be obtained directly from cellobiose octa-acetate.

The results confirm the conclusion already drawn by Ost and Wilkening that the cellulose molecule is built up exclusively from dextrose residues. T. S. P.

Nitrocellulose. H. TEDESCO (*Zeitsch. ges. Schiess-Sprengstoffwesen*, 1912, **7**, 474—477).—An account of numerous experiments on various methods of preparing nitrocellulose, with special regard to the varying nitrogen content and stability of the products obtained under different conditions, such as varying the relative concentrations of the acids employed, the time allowed, and the temperature at which nitration is carried out, and employing different forms of cellulose for the experiments. F. M. G. M.

Soil Humus. SHERMAN LEAVITT (*J. Ind. Eng. Chem.*, 1912, **4**, 601—604).—Two methods of preparing samples of humus are fully described, and the following facts are emphasised.

(1) Two methods were employed for the removal of clay : (*a*) Mooers and Hampton's method; (*b*) mechanical separation, without evaporation to dryness.

(2) Indications were obtained of the relative behaviour of ferric iron, ferrous iron, and calcium in the retention of humus from water solution.

(3) Protein or protein-like substances were present in the humus examined.

(4) A starch-like substance was present which can be hydrolysed by acids, acted on by diastase with subsequent acid hydrolysis, and both processes gave reducing sugars in comparable amounts in all samples of humus examined.

(5) One of these reducing sugars was obtained in crystalline form, but has not yet been fully identified.

(6) Pentosans were present in appreciable amounts in all samples of humus examined.

(7) Nitrogen, present probably as an amino-acid, was found in the 1% hydrochloric acid extract in all soils examined by the official method. F. M. G. M.

Action of Hypochlorous Acid on Tertiary Amines. JAKOB MEISENHEIMER (*Ber.*, 1913, **46**, 1148—1161).—Willstätter and Iglauer (A., 1900, i, 458) have shown that dialkylchloroamines are formed by the action of hypochlorous acid on tertiary amines (compare also Hantzsch and Graf, A., 1905, i, 575). The authors have applied the reaction to simple tertiary amines, and are led to the conclusion that a trialkylamine dichloride is first formed, which rapidly decomposes with elimination of hydrogen chloride according to the scheme for trimethylamine : (i) $N(CH_3)_3 + Cl_2 = N(CH_3)_3Cl_2$;

(ii) $N(CH_3)_3Cl_2 = N(CH_3)_2(:CH_2)Cl + HCl$.

Dimethylmethylene ammonium chloride becomes transformed into formaldehyde and dimethylamine hydrochloride, the latter finally reacting with excess of hypochlorite, yielding dimethylchloroamine. This explanation differs from that given by Willstätter or Hantzsch in that two molecules of hypochlorous acid are required for each molecule of amine instead of one, and thus accounts for the fact that Willstatter and Iglauer obtained the best yields of chloronortropidine only by the use of two or more molecules of hypochlorous acid. Further, it involves the formation of aldehydes instead of alcohols as secondary products, and the production of large quantities of formaldehyde or acetaldehyde during the action of sodium or calcium hypochlorite on trimethylamine or triethylamine has been experimentally proved. Such aldehydes must be directly formed, since, under the conditions employed, alcohols are not oxidised to aldehydes. The assumption of the primary addition of chlorine appears at first sight to be improbable, since free chlorine does not convert tertiary amines into dialkylchloroamines to an appreciable extent. This is explained by the fact that two molecules of a tertiary amine are converted by one molecule of chlorine into a mixture of the hydrochlorides of the tertiary and secondary amines :

$$2N(CH_3)_3 + Cl_2 + H_2O = NMe_2H_2Cl + NMe_3HCl + CH_2O,$$
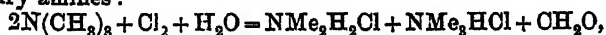
and that free chlorine does not react with salts of amines in the same manner as with the free amines.

No action occurs when the hydrochlorides of trimethylamine or triethylamine are mixed with aqueous solutions of free hypochlorous acid. With the free amines, dialkylchloroamines are formed in small quantity. Good yields of the latter substances can only be obtained by employing sodium hypochlorite or, better, bleaching powder.

An aqueous solution of trimethylamine hydrochloride was added to a cooled suspension of bleaching powder in water. On distillation, a mixture of dimethylchloroamine and methyldichloroamine was obtained, the latter being derived from decomposition of the former. Formaldehyde remained chiefly in the residue, and was identified by precipitation with p-nitrophenylhydrazine. Good yields of chloroamine were only obtained when a large excess of bleaching powder was used. Employment of sodium hypochlorite led to similar results. The yields, however, were uniformly less, and the best experimental conditions less readily ascertained. Nitrogen, nitric acid, and tetramethylammonium chloride were not formed.

Triethylamine hydrochloride in aqueous solution was similarly converted by an aqueous suspension of bleaching powder into a mixture of diethylchloroamine and ethyldichloroamine, which possibly contained a small quantity of chloroform. A large excess of bleaching powder was necessary, since, otherwise, the yields of chloroamine became very small. On the other hand, a portion of the triethylamine became then converted into diethylamine as was shown in experiments with sodium hypochlorite.

Triethylamine hydrochloride did not react with chlorine water, which, however, was decolorised by dimethylamine hydrochloride.

The reaction between triethylamine and chlorine water has been investigated. When the former was distilled into the latter, smaller

quantities of diethylamine hydrochloride and acetaldehyde were obtained than are required by the equation:

$$2NEt_3 + Cl_2 + H_2O = NEt_2HCl + NEt_2H_2Cl + C_2H_4O.$$
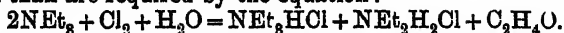
The authors consider that acid is formed in by-reactions which converts the tertiary amine into the corresponding salt, which is not acted on by chlorine. In a subsequent experiment, in which the amine was added in one portion to the chlorine water, a somewhat larger amount of aldehyde was detected.   H. W.

Preparation of Betaine from Molasses Residues. KARL URBAN (*Zeitsch. Zuckerind. Böhm.*, 1913, 37, 339—341).—To obtain betaine the evaporated molasses residues are mixed with an equal volume of concentrated hydrochloric acid. After cooling, the alkali chlorides which have separated are removed by filtration, and the filtrate is evaporated in a porcelain dish. The volatile organic acids and hydrochloric acid pass away, and humus substances are precipitated. These are also filtered off, and the residue further evaporated to a thick syrup. This is dissolved in water, filtered, decolorised by means of charcoal, and concentrated, when betaine hydrochloride separates out in a nearly pure state.   E. F. A.

Chemical Reactions Brought About by Sunlight. DOMENICO GANASSINI (*Chem. Zentr.*, 1913, i, 153—154; from *Giorn. Farm. Chim.*, 1912, 61, 439—444, 481—491).—Aqueous solutions of some mono- and di-basic amino-acids have been exposed to sunlight for three or four days, then treated with an excess of magnesium oxide, and left with red litmus paper. This soon became blue, whereas solutions which had been kept in the dark were without action. It was shown that glycine, alanine, asparagine, aspartic acid, and glutamic acid gradually decomposed into the corresponding aldehyde, ammonia, and carbon dioxide.   J. C. W.

⁍ Synthesis of the Natural Hydroxyproline Present in Proteins. Pyrrolidine Derivatives. IV. HERMANN LEUCHS and JOSEPH F. BREWSTER (*Ber.*, 1913, 46, 986—1000).—The preparation of hydroxyproline has been improved by treating $a\delta$-dichlorovalerolactone with ammonia instead of δ-chloro-a-bromovalerolactone.

γ-Hydroxyproline-(a)-phenylcarbimide is resolved by means of quinine. The synthetic l-γ-hydroxyproline derivative has $[a]_D^{20} - 37 \cdot 0°$, whereas the natural product has $[a]_D^{20} - 37 \cdot 2°$. This synthesis confirms the γ-position of the hydroxy-group and the structure assumed for the natural hydroxyproline.

The phenylcarbimide of hydroxyproline-(b) is also resolved by means of quinine, the ammonium salt having $[a]_D \pm 45°/d$. The active acid could not be obtained crystalline, but the corresponding hydantoins crystallise without difficulty.

To convert the γ-hydroxyproline-phenylcarbimide into the corresponding amino-acid, heating with concentrated hydrochloric acid in a sealed tube at 95° is necessary, but the product has lost its optical activity. To preserve this, the heating is carried out at 95° with aqueous ammonia, when γ-hydroxyproline and phenylcarbamide are

obtained. The synthetic *l*-hydroxyproline has $[a]_D^{20} - 76·3°$, whereas the only value available for the natural acid is $- 81°$.

The *quinine* salt of *hydroxyproline-phenylcarbimide* crystallises in needles or thin prisms, m. p. 206—209° (decomp.), $[z]_D - 37·2°$.

The corresponding *hydantoin* also crystallises in needles or thin prisms, m. p. 122—123°, $[a]_D^{20} - 50·4°$.

l-γ-*Hydroxyproline-phenylcarbimide*-(a) has m. p. 175°.

The corresponding derivative of γ-hydroxyproline-(*b*) does not crystallise, but the *hydantoin* forms lustrous, oblique prisms, m. p. 156—158°, $[a]_D^{20} - 55·2°$.   E. F. A.

A New Amino-acid of the Composition $C_6H_{13}O_2N$ Obtained by the Total Hydrolysis of the Proteins of the Nerve Substance. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1913, **84**, 39—59. Compare A., 1912, ii, 1191).—The leucine fraction of the products of the complete hydrolysis of nerve proteins contains an amino-acid, $C_6H_{13}O_2N$, differing from either leucine,

$$CHMe_2·CH_2·CH(NH_2)·CO_2H,$$
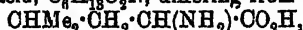
or *iso*leucine, $CHMeEt·CH(NH_2)·CO_2H$, which is regarded as *d*-a-amino-hexoic acid, $CH_3·[CH_2]_3·CH(NH_2)·CO_2H$, and termed caprine. The existence of this isomeride in the nerve proteins was suggested by Thudichum, who did not determine its constitution. It is probable that it is present in other proteins. The ester of *d*-caprine has b. p. 91°/12 mm. d-*Caprine* itself has decomp. 285°, $[a]_D^{20} + 6·53°$ in water, and $+ 14·1°$ in 20% hydrochloric acid, and tastes faintly sweet. The corresponding *hydroxy-acid* crystallises in long, four-angled plates, m. p. 57°, $[a]_D^{20} - 4·68°$. The same acid prepared from the synthetic amino-acid forms slender, needle-shaped prisms, m. p. 60°, $[a]_D^{20} - 2·17°$, whereas the corresponding hydroxy-acid from *l*-leucine has m. p. 71°, $[a]_D^{20} - 16·37°$.   E. F. A.

Compounds of Guanylcarbamide and Guanylguanidine with Dextrose. LEOPOLD RADLBERGER (*Chem. Zentr.*, 1912, ii, 1963—1964; from *Österr. ung. Zeitsch. Zucker-Ind. Landw.*, 1912, **41**, 745—750).—Guanylcarbamide (dicyanodiamidine) forms a *chloride*, $C_2H_7ON_4Cl,\frac{1}{2}H_2O$, which is obtained in thin, colourless leaflets by evaporating the solution in concentrated hydrochloric acid over lime. The aqueous solution is neutral, and when rendered alkaline and boiled with a few drops of copper sulphate solution, develops a violet colour and deposits a rose-red *powder*, $C_4H_6O_2N_4Cu$, on cooling. Guanylguanidine (biguanide), may be purified by recrystallisation from alcohol (compare Bamberger and Dieckmann, A., 1892, 737). The chloride has the formula

$$C_2H_9N_5Cl_2.$$
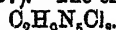
The chlorides condense with dextrose in alcoholic solution. *Guanyl-carbamide-dextrose*,

$$OH·CH_2·[CH·OH]_4·CH:N·C(NH)·NH·CO·NH_2,HCl,$$
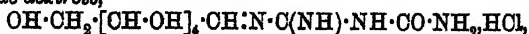
forms slender, microscopic needles, m. p. 107° (decomp.), $a_D^{20} + 0·2°$ (2% solution in alcohol, 2-dcm. tube), which reduce Fehling's solution and respond to the above test for guanylcarbamide. *Guanylguanidine-dextrose*, $OH·CH_2·[CH·OH]_4·CH:N·C(NH)·NH·C(NH)·NH_2,2HCl$, forms small needles which sinter at 116°, have a bitter taste, reduce

Fehling's solution, and give red needles of cuprobiguanide sulphate with ammoniacal copper sulphate. A 2% alcoholic solution in a 2-dcm. tube gives $a_D^{20} + 0.5°$. J. C. W.

Action of Sulphuric Acid on Dicyanodiamide Correction. HJALMAR LIDHOLM (*Ber.*, 1913, **46**, 1218. Compare this vol., i, 252).—The formula for dicyanodiamide was suggested by Bamberger (A., 1883, 907) and not by Pohl, and the reduction to guanidine was accomplished by Bamberger and Seeberger (A., 1893, 494).

J. C. W.

Colour Changes in Solutions of Cobaltous Thiocyanate. RAÚL WERNICKE (*Anal. Soc. Chim. Argentina*, 1913, **1**, 8—32).—Pure cobaltous thiocyanate was obtained by the action of an excess of the sulphate on alcoholic potassium thiocyanate, and repeated extraction and crystallisation of the cobalt salt by alcohol. Data of the conductivity and viscosity are given. The phenomena of colour-change are in general similar to those shown by the chloride. G. D. L.

Reduction of Sodium Nitroprusside by Hydrogen Sulphide. DOMENICO VENDITORI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 162—167. Compare A., 1906, i, 486).—The reduction was effected by the action of an excess of hydrogen sulphide on a 10% solution of sodium nitroprusside kept on a water-bath for five or six hours. Hydrogen cyanide is evolved, and ultimately there results a solution (of nitrosulphide and ferrocyanide) and a precipitate (of sulphur and complex iron cyanogen compounds). As to the soluble products, 100 parts of nitroprusside yield about 13 parts of the nitrosulphide, $NaFe_4(NO)_7S_3$, and about 42 parts of sodium ferrocyanide. The yellowish-white precipitate becomes blue on exposure to the air; the yield of it is about 33% of the nitroprusside taken. When it is treated with warm concentrated hydrochloric acid, a blue powder remains undissolved, whilst the solution contains a green substance which can be re-precipitated with water. It is uncertain whether the acid effects a separation or induces a further reaction. The original crude precipitate seems to have a constant composition. R. V. S.

Vinyl*cyclo*propane and its Derivatives. NICOLAI J. DEMJANOV and M. DOJARENKO (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 176—184). —By various methods Gustavson (A., 1896, i, 669) obtained from vinyltrimethylene an alcohol, b. p. 115—118°. This alcohol is of tertiary character, and from the value of its optical exaltation and from the fact that its boiling point exceeds that of dimethylethyl-carbinol by 15°, which is also the difference between the boiling points of β-methylbutyl alcohol and *cyclo*butylcarbinol, the authors conclude that it is probably 1-methyl*cyclo*butan-1-ol,

$$CH_2{<}^{CH_2}_{CH_2}{>}CMe·OH,$$
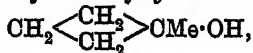
and not 1-ethyl*cyclo*propan-1-ol.

The alcohol is converted by the action of hydriodic acid, first into the iodide, C_5H_9I, b. p. 50°/22 mm., 53°/30 mm., D_4^{18} 1·603, and

subsequently into the iodide, $C_5H_{10}I_2$. Reduction of the iodide C_5H_9I, by means of zinc dust and acetic acid yields (1) *ethyl*cyclo-

propane, $\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>\!CHEt$, b. p. 34—35°/753 mm., D_0^0 0·6973, D_4^0 0·6971,

D_4^{17} 0·6805, n_D^{17} 1·3814, which is also obtained on reducing vinyl*cyclo*-propane by means of hydrogen in presence of platinum black, and (2) an ester, $C_7H_{14}O_2$, of the original alcohol and acetic acid.

<div align="right">T. H. P.</div>

Terpenes and Ethereal Oils. CXIV. Alicyclic Unsaturated Hydrocarbons. OTTO WALLACH (*Annalen*, 1913, 396, 264—284).— 4-Methyl*cyclo*hexan-1-one and magnesium methyl iodide yield by the usual method 1 : 4-dimethyl*cyclo*hexan-1-ol, which is converted by boiling dilute sulphuric acid into 1 : 4-dimethyl-Δ^1-*cyclo*hexene, b. p. 127—128°, $D^{19·5}$ 0·8020, n_D 1·4459. By oxidation with 1% potassium permanganate at 0°, the latter is converted into 1 : 4-*dimethyl*cyclo-*hexane*-1 : 2-*diol*, m. p. 77°, which yields 1 : 4-dimethyl*cyclo*hexan-2-one by treatment with dilute sulphuric acid.   1 : 4-Dimethyl-Δ^1-*cyclo*hexene forms a *nitrosochloride*, m. p. 83—84°, which is easily volatile with

steam, forms a *nitrolpiperidide*, $C_5NH_{10}\cdot CMe\!<\!\begin{matrix}C(:NOH)\cdot CH_2\\CH_2\!-\!\!-\!\!-\!CH_2\end{matrix}\!\!>\!CHMe$,

m. p. 169—170°, and is converted into 1 : 4-dimethyl-Δ^6-*cyclo*hexen-2-oneoxime by loss of hydrogen chloride.

i-1 : 3-Dimethyl*cyclo*hexan-3-ol is converted by boiling dilute sulphuric acid into 1 : 3-*dimethyl*-Δ^3-*cyclohexene*, b. p. 127·5—128·5°, D^{21} 0·8025, n_D^m 1·4466, which forms a *nitrosochloride* (the *nitrolpiperidide* has m. p. 130—131°) extremely slowly, and is oxidised to 1 : 3-dimethyl-*cyclo*hexane-3 : 4-diol by 1% potassium permanganate.

By careful fractional distillation with an efficient column, it can be shown that the liquid obtained by the auto-condensation of methyl-heptenone in the presence of zinc chloride or phosphoric oxide, and hitherto regarded as pure dihydro-*m*-xylene, contains 1 : 3-dimethyl-Δ^3-*cyclo*hexene. Also when methylheptenone is treated with 75% sulphuric acid, the product is shown to be a mixture of 1 : 3-dimethyl-Δ^3-*cyclo*hexene and *m*-xylene.

1 : 2-Dimethyl*cyclo*hexan-1-ol and boiling dilute sulphuric acid yield 1 : 2-dimethyl-Δ^1-*cyclo*hexene, b. p. 135—137° (Sabatier gives 132°), D^{20} 0·824, n_D^{20} 1·4587, which forms a *nitrosochloride*, m. p. 58—60°, colourless when solid, blue when liquid, from which an oxime cannot be obtained. The unsaturated hydrocarbon forms a *dibromide*, m. p. 154—156°, and a *glycol*, m. p. about 38—39°, by oxidation.

[With L. AUGSPURGER.]—By warming with dilute sulphuric acid, 4-methyl-1-ethyl*cyclo*hexan-1-ol yields chiefly 4-*methyl*-1-*ethyl*-Δ^1-cyclo-*hexene*, b. p. 153—154°, D^{22} 0·8145, n_D 1·4514, which forms a *nitroso-chloride* consisting of two stereoisomeric modifications, one having m. p. 103—104° and being sparingly soluble in acetone or petroleum, the other having m. p. 98—99° and being easily soluble. Both modifications yield the same *nitrolpiperidide*, m. p. 134°, and by loss of hydrogen chloride the same *oxime*, m. p. 59—60°. By oxidation with dilute potassium permanganate, 4-methyl-1-ethyl-Δ^1-*cyclo*hexene is

converted into 4-*methyl*-1-*ethylcyclohexane*-1 : 2-*diol*, m. p. 76—77', the constitution of which is proved by its conversion into 4-methyl-1-ethyl*cyclo*hexan-2-one.

[With HANS SCHLUBACH.]—1 : 3 : 5-*Trimethylcyclohexan*-1-*ol*, b. p. 181°, prepared from 3 : 5-dimethyl*cyclo*hexan-1-one and an excess of magnesium methyl iodide, is converted by boiling 50% sulphuric acid into 1 : 3 : 5-*trimethyl*-Δ^1-*cyclohexene*, b. p. 142·5—143·5°, D^{21} 0·7965, n_D^{21} 1·4447, which forms a *nitrosochloride*, m. p. 134° (*nitrolpiperidide*, m. p. 122—123°), and is oxidised to 1 : 3 : 5-*trimethylcyclohexane*-1 : 2-*diol*, m. p. 104°, by cold dilute potassium permanganate.   C. S.

Preparation of Partly Hydrogenised Cyclic Hydrocarbons. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 255538. Compare this vol., i, 349).—When dichloro*cyclo*hexane is heated at 350—450° and 15—20 mm. in the presence of potassium hydroxide, it gives rise to *cyclo*hexadiene, whilst 1 : 2-dibromo*cyclo*hexane furnishes $\Delta^{1.3}$-*cyclo*-hexadiene and chloro*cyclo*pentane yields *cyclo*pentene.   F. M. G. M.

Derivatives of Phenylacetylene, Methoxyphenylacetylene, and Allied Compounds. FRANZ KUNCKELL [with KURT ERAS, EMIL MULLER, and ALFRED HILDEBRANDT] (*Ber. Deut. Pharm. Ges.*, 1913, **23**, 188—227).—A recapitulation and extension of previous work on the preparation of derivatives of phenylacetylene from aryl chloro-methyl ketones (A., 1897, i, 282, 522 ; 1901, i, 75, 552, 638 ; 1903, i, 413).

p-Tolylacetylene combines with bromine to form a *dibromide*, a pale yellow oil, b. p. 139—143°/13 mm., D^{17} 1·669, and a yellow, viscid, oily *tetrabromide* ; with ammoniacal silver nitrate it yields a white, gelatinous *silver* salt, which forms an explosive grey powder when dry. The *copper* salt is light yellow, and is oxidised by aqueous potassium ferricyanide in the presence of potassium hydroxide to *di-p-tolylbuta-di-inene*, $C_7H_7\cdot C\vdots C\cdot C\vdots C\cdot C_7H_7$. This crystallises in white needles, m. p. 183°, and yields a *dibromide*, m. p. 148°, *tetrabromide*, m. p. 163°, and an *octabromide*, m. p. 156—157°.

p-Ethylphenylacetylene gives a yellow oily *dibromide*, b. p. 168—172°/20 mm., D^{18} 1·598, a *tetrabromide*, and greenish-grey *silver* salt ; the *copper* salt forms a light yellow powder, and is oxidised by alcoholic potassium ferricyanide to *di-p-ethylphenylbutadi-inene*, white needles, m. p. 72°.

αβ-Dichloro-2-bromo-5-methoxystyrene, $OMe\cdot C_6H_3Br\cdot CCl\vdots CHCl$, pre-pared from 2-bromo-5-methoxyphenyl chloromethyl ketone and phosphorus pentachloride, forms a yellowish-brown oil, b. p. 210—215°/25 mm., D^{18} 1·3610. When heated with phosphorus pentachloride on the water-bath, 3 : 4-dichloroacetyl-1-methoxybenzene gives rise to 1-*methoxy*-3 : 4-*bis-αβ-dichlorovinylbenzene*, $OMe\cdot C_6H_3(CCl\vdots CHCl)_2$, a pale yellow liquid, b. p. 160—170°/17 mm., D^{21} 1·461 ; if the reaction is carried out at a higher temperature, 2 : 5-*dichloro*-1-*methoxy*-3 : 4-*bis-αβ-dichlorovinylbenzene*, $OMe\cdot C_6HCl_2(CCl\vdots CHCl)_2$, a yellow oil, b. p. in vacuum 170—180°, D^{19} 1·570, is produced.

$\alpha\beta$ 2 : 5-*Tetrachloro*-4-*methoxystyrene*, OMe·C$_6$H$_2$Cl$_2$·CCl:CHCl, prepared by boiling *p*-methoxyphenyl chloromethyl ketone with excess of phosphoius pentachloride, is a yellow liquid of aromatic odour, b. p. 165—175°/18 mm., D^{17} 1·44; the prolonged action of phosphorus pentachloride gives rise to $\alpha\beta$ 2 : 3 : 5-*pentachloro*-4-*methoxystyrene*, a yellow oil which has b. p. 180—190°/20 mm., D^{18} 1·6100, and solidifies when kept.

$\alpha\beta$-*Dichloro*-p-*ethoxystyrene*, prepared from *p*-ethoxyphenyl chloromethyl ketone, is a brownish-yellow liquid of disagreeable odour, b. p. 170—180°/26 mm., D^{20} 1·243.

5-Methoxy-*o*-tolyl chloromethyl ketone gives rise to $\alpha\beta$-*dichloro*-5-*methoxy*-2-*methylstyrene*, OMe·C$_6$H$_2$Me·CCl:CHCl, a pale yellow oil, b. p. 160°/20 mm., D^{18} 1·2520; *chloro*-5-*methoxy*-o-*tolylacetylene* has b. p. 145—150°/15 mm., D^{18} 1·166. 5-*Methoxy*-o-*tolylacetylene* is a pale yellow liquid of ethereal odour, b. p. 110—120°/18 mm., D^{17} 1·011.

2 : 4-*Dimethoxyphenyl chloromethyl ketone*, prepared from resorcinol dimethyl ether and chloroacetyl chloride, crystallises in yellow leaflets, m. p. 104°, and yields with phosphorus pentachloride, $\alpha\beta$-*dichloro*-2 : 4-*dimethoxystyrene*, a reddish-yellow liquid which has a sweet odour and becomes crystalline when kept, b. p. 160—165°/18 mm.

Resorcinol diethyl ether and chloroacetyl chloride yield 4 : 4(?)-*dichloroacetyl*-1 : 3-*diethoxybenzene*, C$_6$H$_2$(OEt)$_2$(CO·CH$_2$Cl)$_2$, small, yellow needles, m. p. 106°.

Di-p-*chloroacetyldiphenyl ether*, O(C$_6$H$_4$·CO·CH$_2$Cl)$_2$, prepared from diphenyl ether and chloroacetyl chloride, forms greenish granules, m. p. 111°, and gives rise to *di*-p-$\alpha\beta$-*dichlorovinyldiphenyl ether*, O(C$_6$H$_4$·CCl:CHCl)$_2$, a viscid liquid having a green shimmer, b. p. 225°/20 mm.

2 : 6-Dichloroacetyl mesitylene, from chloroacetyl chloride and mesitylene, forms large, lustrous crystals, m. p. 134—135° (compare Meyer, A., 1897, i, 55), and yields 1 : 3 : 5-*trimethyl*-2 : 6-*bis*-$\alpha\beta$-*dichlorovinylbenzene*, C$_6$HMe$_3$(CCl:CHCl)$_2$, a colourless oil, b. p. 180—181°/12 mm., D^{18} 1·3106. When impure, the last-named substance gradually loses hydrogen chloride on exposure to air, yielding a white *substance*, m. p. 95°.

2 : 4 : 6-*Triethylphenyl chloromethyl ketone*, prepared from 2 : 4 : 6-triethylbenzene, is a strongly refractive liquid, b. p. 207—215°/20 mm., and yields $\alpha\beta$-*dichloro*-2 : 4 : 6-*triethylstyrene*, which forms a golden-yellow oil of aromatic odour, b. p. 175°/18 mm., D^{18} 1·1447; 2 : 4 : 6-*triethylphenylchloroacetylene*, a yellow oil, b. p. 155°/18 mm., D^{18} 1·0236; 2 : 4 : 6-*triethylphenylacetylene*, a colourless liquid, b. p. 124—126°/14—16 mm., D^{21} 0·9004, which forms a yellow, amorphous *copper* salt.

2 : 6-*Dichloroacetyl*-1 : 3 : 5-*triethylbenzene*, C$_6$HEt$_3$(CO·CH$_2$Cl)$_2$, crystallises in transparent, hexagonal plates, m. p. 71—72°, and gives rise to 1 : 3 : 5-*triethyl*-2 : 6-*di*-$\alpha\beta$-*dichlorovinylbenzene*, C$_6$HEt$_3$(CCl:CHCl)$_2$, a golden-yellow oil, b. p. 210—215°/17—18 mm., D^{18} 1·245.

2 : 4-*Di*-*chloroacetyl*-6-*acetyl*-1 : 3 : 5-*triethylbenzene*,

$$\text{COMe·C}_6\text{Et}_3(\text{CO·CH}_2\text{Cl})_2,$$

from 2 : 4 : 6-triethylphenyl methyl ketone and chloroacetyl chloride, crystallises in stout, transparent needles, m. p. 72°.   F. B.

Preparation of Sulphonic Acids of the Benzene and Naphthalene Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 255724. Compare Friedländer and Lucht, A., 1894, i, 138). —When an electric current is passed through an alkaline solution of an aniline-, naphthylamine- or naphthol-polysulphonic acid in the presence of sodium amalgam a sulphonic group is eliminated.

The reduction of the following compounds is described : aniline-3 : 6-disulphonic acid to aniline-3-sulphonic acid ; α-naphthylamine-4 : 8-disulphonic acid to α-naphthylamine-4-sulphonic acid ; β-naphthylamine-4 : 8-disulphonic acid to the corresponding -8-sulphonic acid ; β-naphthylamine-5 : 7-disulphonic acid to β-naphthylamine-7-sulphonic acid ; α-naphthylamine- 3 : 5 : 7-trisulphonic acid to α-naphthylamine-3 : 7-disulphonic acid ; α-naphthylamine-2 : 4 : 6-trisulphonic acid to α-naphthylamine-2 : 4-disulphonic acid ; α-naphthylamine-2 : 5 : 7-trisulphonic acid to α-naphthylamine-2 : 7-disulphonic acid ; α-naphthol-3 : 8-disulphonic acid to α-naphthol-3-sulphonic acid ; α-naphthol-2 : 4 : 8-trisulphonic acid to α-naphthol-2 : 4-disulphonic acid, and β-naphthol-3 : 6 : 8-trisulphonic acid to β-naphthol-3 : 6-disulphonic acid.

F. M. G. M.

Δ^1-Dihydronaphthalene. FRITZ STRAUS (*Ber.*, 1913, 46, 1051—1055).—By the exhaustive methylation of tetrahydro-β-naphthylamine, Willstätter and King (this vol., i, 353) have obtained a dihydronaphthalene which they consider to be identical with the Δ^2-dihydronaphthalene, described by Bamberger (A., 1896, i, 99).

The author points out, however, that the properties of Willstätter and King's dihydro-compound show such complete agreement with those of the Δ^1-dihydronaphthalene (this vol., i, 256) that there can be no doubt as to the identity of the two hydrocarbons.

Δ^2-Dihydronaphthalene forms a dibromide differing very little in m. p. from that of the Δ^1-isomeride. The removal of bromine by means of zinc in alcoholic solution yields in each case the original hydrocarbon. The statement of Willstätter and King that their dihydronaphthalene can be obtained by the removal of bromine from the dibromide of Bamberger's Δ^2 dihydro-compound is, therefore, erroneous.

F. B.

Halogen Compounds of Anthracene. KURT H. MEYER and KARL ZAHN (*Annalen*, 1913, 396, 166—180).—The halogen additive compounds of anthracene are derivatives of 1 : 2 : 3 : 4-tetrahydroanthracene. Attempts to replace the halogen atoms by hydroxyl, amino-, and other groups have been unsuccessful, but a new case of isomerism has been observed.

Graebe and Liebermann have shown that the action of bromine vapour on anthracene yields 9 : 10-dibromoanthracene tetrabromide. This yields 1 : 3 : 9 : 10-tetrabromoanthracene by treatment with alcoholic potassium hydroxide, 2 : 9 : 10-tribromoanthracene by heating, and 9 : 10-dibromoanthracene by reduction with zinc and acetic acid.

By treating anthracene moistened with chloroform with bromine (4 mols.) in chloroform, a *substance*, $C_{14}H_9Br_9$, m. p. 134—135° (decomp.), colourless needles, is obtained, which reacts like the older isomeride towards alcoholic potassium hydroxide, heating, and reducing agents. The two isomerides, therefore, are structurally alike. It is suggested that the two are stereoisomeric, the new compound, which is called a-9 : 10-*dibromoanthracene tetrabromide*, having the four homonuclear bromine atoms in *cis*-positions, whilst in the older (β-) compound they are alternately *cis* and *trans*. These configurations are in harmony with a property which is characteristic of the a-, but not of the β-isomeride. a-9 : 10 Dibromoanthracene tetrabromide in boiling benzene is decomposed into bromine and 9:10-dibromoanthracene by exposure to sunlight or to the light of a mercury lamp; the change is not reversible in boiling benzene in darkness.

a-9:10-*Dichloroanthracene tetrabromide*, $C_{14}H_8Cl_2Br_4$, m. p. 141—142° (decomp.), colourless, hexagonal prisms, prepared from dichloroanthracene and bromine (2 mols.) in chloroform, exhibits a similar photochemical decomposition in benzene, whilst the long-known β-isomeride does not.

The 9:10-dichloroanthracene tetrachloride obtained by Hammerschlag by passing chlorine into a benzene solution of anthracene is the β-isomeride, since it is photochemically inactive and does not liberate iodine from potassium iodide. The a-isomeride has not been obtained. The β-isomeride yields 1 : 3 : 9 : 10-tetrachloroanthracene (the constitution of which is proved by its conversion into 1 : 3-dichloroanthraquinone) by treatment with alcoholic potassium hydroxide, 2 : 3 : 9 : 10-*tetrachloroanthracene*, m. p. 240—241°, yellow needles (yielding 2 : 3-dichloroanthraquinone by oxidation), by heating above its m. p., and 9 : 10-dichloroanthracene by reduction with zinc and acetic acid.

9 : 9 : 10 : 10-Tetrachloroanthracene, m. p. 170° (Schwarzer gives 149—150°), obtained together with 9 : 10-dichloroanthracene tetrachloride by passing chlorine into a chloroform solution of anthracene at 0°, yields the *dianil*, $NPh:C{<}^{C_6H_4}_{C_6H_4}{>}C:NPh$, m. p. 201—202°, golden-yellow leaflets, with aniline in boiling alcohol, and the *tetramethylacetal*, $C(OMe)_2{<}^{C_6H_4}_{C_6H_4}{>}C(OMe)_2$, m. p. 161—162°, colourless crystals, with boiling methyl alcohol and sodium carbonate.

O. S.

Preparation of o-Substituted Derivatives of Acetoacetanilide and Their Homologues.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 256621).—3-*Chloroacetoaceto-o-toluidide*, colourless needles, m. p. 120°, is obtained in 66% yield when a solution of ethyl acetoacetate in chlorobenzene is added to a hot solution of 3-chloro-o-toluidine in the same solvent.

o-*Chloroacetoacetanilide* is prepared in 75% yield in a similar manner from o-chloroaniline.

Acetoaceto-o-anisidide, a colourless, crystalline powder, has m. p. 84°,

whilst the analogous *compounds* from 3-amino-*p*-tolyl ethyl ether and from *phenyl* o-*aminophenyl ether* have m. p. 80° and 61° respectively.

F. M. G. M.

The Manufacture of Tetranitromethylaniline. F. LANGENSCHEIDT (*Zeitsch. ges. Schiess-Sprengstoffwesen*, 1912, **7**, 445—447).—2 : 4 : 6-N-*Tetranitromethylaniline* ("Tetril") (annexed formula), m. p. 129—130°, is obtained in 87% yield when pure methyl- or dimethyl-aniline is dissolved in 10 parts of concentrated sulphuric acid (pure and free from lead), thoroughly cooled, and slowly added to 4·3 parts of nitric acid (47° Bé') at 40°, 44° being the utmost limit to which the temperature may rise in the early stages of the operation; later, when the violence of the action decreases, it is allowed to rise to, and maintained at, about 53—55°, and after about eleven hours the nitration is completed. The product is purified by crystallisation from benzene.
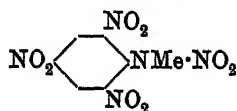
F. M. G. M.

[**Preparation of 4-Chloro-2 : 6-diaminophenol.**] FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 256794).—4-*Chloro*-2 : 6-*diaminophenol*, obtained by the reduction of 4-chloro-2 : 6-dinitrophenol, crystallises from hot water in needles, has m. p. 88—89°, and furnishes crystalline *salts*.

3 : 5-*Diamino*-p-*cresol*, m. p. 146°, is prepared by the reduction of the corresponding 3 : 5-dinitro-*p*-cresol.

F. M. G. M.

Preparation of Dialkylaminoformic Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 255942).—When halogen formic esters are treated with trialkylamines the following reaction takes place : $ClCO_2R + NMe_3 = NMe_3Cl \cdot CO_2R$, and the compounds so obtained when heated give rise to dialkylaminoformic esters of the general formula : $NMe_3Cl \cdot CO_2R = NMe_2 \cdot CO_2R + MeCl$ (R may be alkyl, aryl, or alkylaryl).

Phenyl dimethylaminoformate, $NMe_2 \cdot CO_2Ph$, colourless needles, m. p. 44—45°, b. p. 134—135°/16 mm., is obtained in quantitative yield when a cooled benzene solution of trimethylamine is slowly treated with phenyl chloro-formate; the intermediate *compound*, $NMe_3Cl \cdot CO_2Ph$, separates as a colourless, crystalline precipitate, and, on subsequently boiling, the reaction mixture is slowly converted into the foregoing ester.

Tolyl dimethylaminoformate, $NMe_2 \cdot CO_2 \cdot C_6H_4Me$, a viscid, colourless oil, b. p. 145—195°/15 mm., consisting of a mixture of the ortho-, meta-, and para-isomerides, is prepared in a similar manner from the mixture of *tolyl chloroformates*, b. p. 85—105°/18 mm., obtained by the action of carbonyl chloride on a freshly distilled benzene solution of crude cresol (b. p. 190—206°) in the presence of dimethylaniline.

β-Naphthyl chloroformate, colourless prisms, m. p. 57° (prepared from carbonyl chloride and β-naphthol), when treated with trimethylamine furnishes the *compound*, $NMe_3Cl \cdot CO_2 \cdot C_{10}H_7$, as a colourless, crystalline precipitate, and on boiling is converted into *β-naphthyl dimethylaminoformate*, $NMe_2 \cdot CO_2 \cdot C_{10}H_7$, colourless crystals, m. p. 92°.

iso*Amyl dimethylaminoformate*, $Me_2N \cdot CO_2 \cdot C_5H_{11}$, a colourless oil, b. p. 194—197°, and *phenyl diethylaminoformate*, $NEt_2 \cdot CO_2Ph$, a colourless oil, b. p. 142—146°/13 mm , are prepared in a similar manner.

<div align="right">F. M. G. M.</div>

Preparation of Aromatic Selenocyano-compounds. FARB-WERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 255982).—An account of the preparation of compounds previously described by Bauer (this vol., i, 263); the m. p. of *o*-nitrophenyl selenocyanate is given as 144—145° (*loc. cit.*, 142°).   F. M. G. M.

Iron Compounds of Phenols. IV. RUDOLF F. WEINLAND and KARL BINDER (*Ber.*, 1913, **46**, 874—885).—The dark blue substance obtainable from catechol and ferric acetate, which dissolves in water to a green solution, was provisionally regarded as having the structure $Fe_3(C_6H_4O_2)_4 \cdot OH, 7H_2O$ (A., 1912, i, 445), but it is now shown to yield acetic acid when warmed, and to contain actually one atomic weight of iron to a molecular weight of acetic acid and of catechol; it is obtained when two molecular proportions of ferric acetate are mixed with 1—2 of catechol in aqueous solution. If, however, four times the above quantity of catechol is used the violet acid, $H\begin{bmatrix} Fe(C_6H_4O_2)_2 \\ H_2O \end{bmatrix}, H_2O$ (*loc. cit.*), is obtained. It is therefore a probable conclusion that the substance which yields a green solution is a complex salt containing as components the above violet acid and the hexa-acetotriferric base (Weinland and Gussmann, A., 1910, i, 457), the constitution accordingly being :

$$[Fe_3(OAc)_6][Fe(C_6H_4O_2)_2]_3, 12H_2O.$$
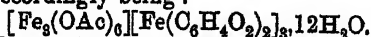
The view is confirmed by the production of a green colour on the addition of the red solution of ferric acetate to a solution of an alkali salt of the above violet acid, or on the addition of a little catechol to ferric acetate solution. It is suggested that the green coloration produced by ferric chloride solution with catechol may be due to the formation of some analogous complex salt. The green colour of the solutions of the above complex salt is not due to the mere superposition of the colours of the acid and metallic radicles, but the possibility is not excluded that some decomposition may occur during the process of solution with formation of still unknown complexes.

The preparation of the violet acid can be effected without the addition of sodium acetate (compare A , 1912, i, 445), provided that sufficient catechol is added to decompose all the ferric acetate.

As ferric chloride is soluble in certain organic solvents, the reaction of this substance with catechol was examined in other solvents than water. In ethereal solution the reaction product was a crystalline, blackish-brown *substance*, $Fe(O \cdot C_6H_4 \cdot OH)Cl_2, Et_2O$ (compare A., 1912, i, 850), which may possibly be an oxonium salt of ether with the acidic portion of the substance; it is very sensitive to moisture, and soon becomes decomposed in the air; in alcohol it gives a blue solution. The reaction in acetophenone solution yields a product which when precipitated by pyridine forms bluish-black, microscopic leaflets of a

substance which may be regarded as a pyridine salt of the acid present in the last substance, that is, $(C_5H_5N)_4.[HFe(C_6H_4O_2)Cl_2]_4$. In pyridine solution a bluish-black, crystalline powder consisting of microscopic leaflets is obtained; the structure of this substance may be that of a salt of the red acid, $H_3[Fe^{III}(C_6H_4O_2)_3]$ (A., 1912, i, 445), with complex bases, and the formula $Fe(C_6H_4O_2)_3 < \genfrac{[}{]}{0pt}{}{Fe(C_5H_5N)_4Cl.H_2O}{Fe(C_5H_5N)_3Cl_2,H_2O}$ is suggested.

The potassium salt of the violet acid retains its molecule of water in a vacuum over sulphuric acid for six months, and the potassium salt of the red acid holds its $2H_2O$ equally tenaciously; the sodium salt of the latter acid, however, yields 8 of its 9 H_2O under similar treatment.

D. F. T.

Some Additive Products of Styphnic Acid. CLAUDIO AGOSTINELLI (*Gazzetta*, 1913, **43**, i, 124—128).—The additive compound of 3:5-*dimethylpyrazole* and styphnic acid,

$$C_5H_8N_2,C_6H_3O_8N_3,$$
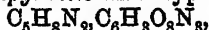
crystallises in golden-yellow scales, m. p. 203—204°. The compound from *antipyrine*, $C_{11}H_{12}ON,C_6H_3O_8N_3$, crystallises in canary-yellow laminæ, m. p. 204°. The compound from *pyramidone*,

$$C_{13}H_{17}ON_3,C_6H_3O_8N_3,$$
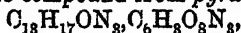
forms thin, yellow needles, m. p. 191°. The compound from *camphorphenylhydrazone*, $C_{10}H_{16}{:}N{\cdot}NHPh,C_6H_3O_8N_3$, crystallises in green, woolly needles, m. p. 150—151°. The compound from *acetonephenylhydrazone*, $C_9H_6{:}N{\cdot}NHPh,C_6H_3O_8N_3$, crystallises in yellowish-green scales, m. p. 104—106°. The compound from *cinnamaldehydephenylhydrazone*, $C_{15}H_{14}N_2,(C_6H_3O_8N_3)_2$, forms minute, pale green needles, m.p. 137—138°. The compound from *benzylidene-aniline*, $C_{13}H_{11}N,C_6H_3O_8N_3$, crystallises in pale yellow scales, m. p. 193°. The compound from *cinnamylideneaniline*,

$$C_{15}H_{13}N,C_6H_3O_8N_3,$$
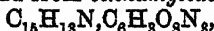
crystallises in bright red laminæ, m. p. 178°. The compound from *benzylideneazine*, $C_{14}H_{12}N_2,C_6H_3O_8N_3$, forms yellow needles, m. p. 152°. The compound from *cinnamylideneazine*, $C_{18}H_{16}N_2,C_6H_3O_8N_3$, crystallises in orange-yellow needles, m. p. 176°.

R. V. S.

Preparation of 2:3-Dihydroxytoluene. SACCHARIN-FABRIK AKTIENGESELLSCHAFT VORM. FAHLBERG, LIST & CO. (D.R.-P. 256345).— 2:3-Dihydroxytoluene, m. p. 68°, b. p. 241° or 112°/3 mm., as obtained by Limpach (A., 1892, 447) had m. p. 47°, and the following method of preparation is now described. *o*-Cresol is sulphonated, and the *o*-cresol-5-sulphonic acid so obtained, chlorinated, when it yields 3-*chloro-o-cresol*-5-*sulphonic acid* (annexed formula); this when heated at 130° with dilute sulphuric acid gives rise to 3-*chloro-o-cresol*, m. p. 185°, or if fused for 8—10 hours at 160—170° with sodium hydroxide and again subsequently heated at 200° with water under pressure, it yields 2:3-dihydroxytoluene in glistening, colourless leaflets.
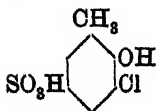
F. M. G. M.

Some New Polymerides of the Phenols with Propenylic Side-chains. ERNESTO PUXEDDU (*Gazzetta*, 1913, 43, i, 128—133).— The author has obtained new polymerides of *iso*safrole and anethole by methods based on the employment of an anhydrous ethereal solution of ferric chloride.

When an anhydrous ethereal solution of *iso*eugenol and ferric chloride is treated with dry hydrogen chloride for three hours, the di*iso*eugenol already known is produced.

If an absolute ethereal solution of *iso*safrole and ferric chloride is treated with dry hydrogen chloride for five days, a new *polymeride* of *iso*safrole is produced ; it crystallises in spherical nodules, m. p. 92°, and reacts with bromine with evolution of hydrogen bromide and formation of an oily product.

Anethole, when treated in a manner similar to that described in the two preceding cases, yields a new *polymeride*, which, however, is better prepared by simply mixing anhydrous ethereal solutions of anethole and ferric chloride ; the mixture deposits a white powder, which does not melt at 340°.   R. V. S.

Action of Nitrous Acid on Ethyl*iso*eugenol. ERNESTO PUXEDDU (*Gazzetta*, 1913, 43, i, 133—138. Compare A., 1912, i, 186).—The paper deals with the ethyl*iso*eugenol peroxide previously described (*loc. cit.*) with a view to showing its analogy to similar substances investigated by Angeli and others (A., 1893, i, 261, 263 ; 1894, i, 72 ; 1895, i, 35). When the peroxide is boiled with alcoholic potassium hydroxide for a few minutes, it is converted into a *substance*, $C_{12}H_{14}O_4N_2$, which crystallises in long, yellow, prismatic needles, which become red at 170°, m. p. 180° (decomp.).

Reduction of the peroxide with tin and hydrochloric acid yields a furazan derivative, $C_{12}H_{14}O_3N_2$, m. p. 116°. When the reduction is effected by zinc and acetic acid in certain conditions, *ethyliso*eugenol-*a*-dioxime, $C_{12}H_{16}O_4N_2$, is produced ; it forms lustrous scales, m. p. 150°. On heating at 150° for some hours, it yields the *β-dioxime*, which forms prismatic crystals, m. p. about 190°.   R. V. S.

Some Derivatives of Hydroxyquinol. IX. GUIDO BARGELLINI (*Gazzetta*, 1913, 43, i, 164—175. Compare Bargellini and Avrutin, A., 1911, i, 68).—The paper deals with the constitution of two sub-stances obtained by the action of zinc chloride on triacetylhydroxy-quinol, and described in the paper cited.

The red substance of m. p. 200—202° is 2 : 4 : 5-*trihydroxyaceto-phenone*, for it is formed by the saponification of the white substance of m. p. 165—166°, and it also results from the action of potassium persulphate on resacetophenone in alkaline solution (compare Bargellini and Aureli, A., 1911, i, 855). Benzoyl chloride yields 2 : 4 : 5-*tri-benzoyloxyacetophenone* with both substances ; it forms colourless needles, m. p. 131—133°. Acetyl chloride gives with both red and white compounds a substance of the empirical formula C_8H_2O, m. p. 110—111°, which is 2 : 4 : 5-*triacetoxyacetophenone*. Both red and white compounds yield diacetyl-β-methylæsculetin (Bargellini and Martegiani, A., 1912, i, 292) when heated with acetic anhydride and

sodium acetate ; the formation of another substance, which begins to decompose at 245°, was also observed.   The reactions above described, taken in conjunction with the results of the molecular weight determination and of the estimation of saponifiable acetic acid in the compound, show that the white substance is a *hydroxydiacetoxy-acetophenone*.

The reaction between zinc chloride and triacetylhydroxyquinol thus results in a migration of one of the acetyl groups to a carbon atom of the nucleus.   Other similar reactions are known.   R. V. S.

Behaviour of Individual Organo-magnesium Compounds Towards Aromatic Ethers. VLADIMIR V. TSCHELINCEV and B. V. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 289—300. Compare A., 1906, ii, 334, 335 ; A., 1907, i, 499 ; A., 1908, i, 254 ; Stadnikov, and also Stadnikov and Kuzmina-Aron, A., 1912, i, 971). —The authors have investigated the products formed and the thermal changes involved in the action of magnesium propyl iodide on (1) benzyl ethyl ether ; (2) diphenylmethyl ethyl ether, and (3) triphenylmethyl ethyl ether.   The products are (1) phenylbutane, *s*-diphenylethane, benzene, and ethyl alcohol ; (2) diphenylbutane and *s*-tetraphenylethane, and (3) triphenylmethane and ethyl alcohol.   The heat effects observed also indicate, not merely a combination of the ether with the organo-magnesium compound, but a more profound interaction.

These results show that when ethers of the aromatic series, which are less stable than the corresponding ones of the aliphatic series, react with organo-magnesium compounds, they are partly divided at the junction of the aromatic radicle with the oxygen of the alkoxy-group.   This division leads to the formation of aromatic hydrocarbons of two types : (1) CH_2PhPr, $CHPh_2Pr$, CPh_3Pr, and (2)

$$CH_2Ph\cdot CH_2Ph,$$
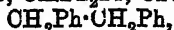
$CHPh_2\cdot CHPh_2$, $CPh_3\cdot CPh_3$.   These hydrocarbons are produced in accordance with the scheme advanced by Erlenmeyer, jun.: (1) $R\cdot OEt + 1Mg\cdot Pr = R\cdot Pr + OEt\cdot MgI$, and (2) $2R\cdot OEt + 2IMg\cdot Pr = R\cdot R + Pr\cdot Pr + 2OEt\cdot MgI$.

Since these hydrocarbons represent the actual products of the interaction of organo-magnesium compounds and ethers, and are not formed only after the action of water on these products, any attempt to draw conclusions concerning the structure of the ethereal complexes of organo-magnesium compounds on the basis of experimental results of this kind is pure speculation.

Further, no certain conclusions can be deduced from consideration of the products obtained by decomposition of the complexes by means of carbon dioxide (compare Stadnikov and Kuzmina-Aron, A., 1912, i, 971), since such decomposition is not quantitative, especially when molecular proportions of the ether and organo-magnesium compound are taken, and at the same time there is no exclusion of the possibility of formation from undecomposed magnesium alkyl iodide of the corresponding fatty acid, and hence of, for example, triphenylacetic acid.

In deciding between the two structures: R_2:$O(MgR)I$ and
$$R_2\text{:}O(MgI)R,$$
it must be borne in mind that ethereal complexes of this type are
obtained, not only with such compounds as MgRI, but also with
magnesium iodide, and in the latter case the only possible structure is
R_2:OI·Mg·OI:R_2.   T. H. P.
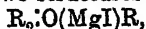
Reduction by means of Organo-magnesium Compounds.
ALEXANDER I. GORSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 163—166).
—The author has previously (A., 1912, i, 622) expressed the opinion
that the formation of triphenylmethane by the interaction of triphenyl-
methyl ethyl ether, propyl iodide, and magnesium in an indifferent
solvent is due to hydrolytic decomposition of the ether into triphenyl-
methyl iodide and reduction of the latter to the corresponding
hydrocarbon. As alkyl iodides and magnesium, however, react in absence
of an ether or other catalyst, it may be that in the above case no
etherate of the type Pr·Mg·OEt is formed, but that these reactions
take place between the individual organo-magnesium compounds and
the ether.

In order to test the accuracy of this view, experiments were made
in which the triphenylmethyl ethyl ether was replaced by other
oxygenated compounds, such as ketones. The reaction between
β-benzopinacolin and magnesium propyl iodide in toluene solution
proceeds in the same direction as the reaction with triphenylcarbinol
in presence of ethyl ether, giving a compound apparently identical
with benzopinacolin alcohol. Similarly, benzophenone yields benz-
hydrol and other compounds. It is known that the action of organo-
zinc compounds on aldehydes and on ketones may, under certain
experimental conditions and with certain radicles in the organo-
metallic compounds, result in the reduction of the aldehydes to
primary, and of the ketones to secondary, alcohols ; hence the
reaction with β-benzopinacolin may be represented by the equation :
$$CPh_3 \cdot COPh + MgPrI = CPh_3 \cdot CHPh \cdot OMgI + C_3H_6.$$
That the reaction between nascent organo-magnesium compounds
and ketones is not generally limited to such a reduction is, however,
rendered evident by the fact that the secondary alcohol is not the sole
final product.

These considerations indicate the possibility that the reaction
between triphenylmethyl ethyl ether and magnesium propyl iodide
may be one of direct reduction, without intermediate formation of
iodide : $CPh_3 \cdot OEt + MgPrI = CHPh_3 + OEt \cdot MgI + C_3H_6$.   T. H. P.

Phenylethanolamines, Phenylnitroethanols, and their Hydr-
oxy-derivatives. KARL W. ROSENMUND (*Ber.*, 1913, **46**, 1034—1050.
Compare A., 1910, i, 106 ; 1911, i, 34).—An account of a preparation
of a number of β-hydroxy-β-arylethylamines, $OH \cdot CHR \cdot CH_2 \cdot NH_2$, by the
reduction of the corresponding nitro-alcohols, $OH \cdot CH \cdot CHR \cdot CH_2 \cdot NO_2$.
The latter compounds are obtained in good yield by decomposing the
sodium salts, produced by the condensation of aromatic aldehydes with
nitromethane in the presence of sodium methoxide, with acetic acid.
On treatment with mineral acids or when heated, the nitro-alcohols

lose water with the formation of the corresponding nitrostyrenes, R·CH:CH·NO₂. They dissolve in alkalis, yielding colourless solutions from which acetic acid liberates the nitro-alcohols unchanged, whilst mineral acids give rise to β-nitrostyrenes.

When dissolved in alkalis and the solutions acidified with acetic acid, the β-nitrostyrenes combine with water to form nitro-alcohols.

A similar addition of alcohol, resulting in the formation of nitro-ethers of the type OEt·CHR·CH₂·NO₂, may be effected by treating the nitrostyrenes with alcoholic alkali hydroxides and subsequently acidifying with acetic acid.

Although hydroxybenzaldehydes do not directly condense with nitromethane, the preparation of the corresponding nitrostyrenes and nitro-alcohols may be readily accomplished by the method illustrated in the following example: p-hydroxybenzaldehyde is converted into p-ethylcarbonatobenzaldehyde (I), CO₂Et·O·C₆H₄·CHO, which instantly reacts with nitromethane in the presence of alkali, yielding the salt CO₂Et·O·C₆H₄·CH(OH)·CH:NO·OK; on treatment with hydrochloric or acetic acid this yields the compounds (II)

$$CO_2Et·O·C_6H_4·CH:CH·NO_2$$
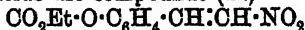
and (III) CO₂Et·O·C₆H₄·CH(OH)·CH₂·NO₂ respectively. If excess of alkali is employed and the reaction mixture allowed to remain for one to two minutes, the carbethoxy-group is removed and subsequent acidification yields (IV) OH·C₆H₄·CH:CH·NO₂ or (V)

$$OH·C_6H_4·CH(OH)·CH_2·NO_2,$$
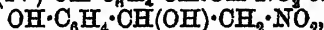
accordingly as hydrochloric or acetic acid is employed.

β-*Nitro-a-phenylethyl alcohol*, OH·CHPh·CH₂·NO₂, prepared by condensing benzaldehyde with nitromethane in alcoholic solution by means of sodium methoxide below 8° and acidifying the aqueous solution of the resulting sodium salt with dilute acetic acid, is a yellow oil, b. p. 163—165°/15 mm. On treatment with sodium methoxide in methyl-alcoholic solution, β-nitrostyrene yields a colourless solution, from which the successive addition of acetic acid and water liberates β-*nitro-a-phenylethyl methyl ether*, OMe·CHPh·CH₂·NO₂, as a pale yellow oil, b. p. 140—141°/15 mm.

β-*Nitro-a-p-methoxyphenyl ethyl alcohol*, OMe·C₆H₄·CH(OH)·CH₂·NO₂, prepared by acidifying with acetic acid an aqueous solution of the *sodium* salt, obtained by the condensation of anisaldehyde and nitromethane with sodium methoxide, is a yellow oil, which partly decomposes on distillation or on treatment with mineral acids into β-nitro-p-methoxystyrene.
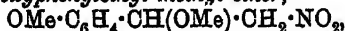
β-*Nitro-a-*p-*methoxyphenylethyl methyl ether*,
$$OMe·C_6H_4·CH(OMe)·CH_2·NO_2,$$
is a yellow oil.

p-Benzyloxybenzaldehyde condenses with nitromethane, yielding β-*nitro-*p-*benzyloxystyrene*, C₇H₇·O·C₆H₄·CH:CH·NO₂, m. p. 120°, from which β-*nitro-a-*p-*benzyloxyphenylethyl methyl ether*,
$$C_7H_7·O·C_6H_4·CH(OMe)·CH_2·NO_2,$$
m. p. 105—106°, is obtained in the usual manner.
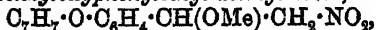
p-*Benzoyloxybenzaldehyde*, prepared by the successive addition of the theoretical amount of potassium hydroxide and benzoyl chloride to an alcoholic solution of p-hydroxybenzaldehyde, yields with nitromethane

β-nitro-p-*benzoyloxystyrene*, which crystallises in slender, pale yellow needles, m. p. 153—155°. *β-Nitro-a-p-benzoyloxyphenylethyl alcohol* forms almost white, lustrous scales, m. p. 127—130°, and yields a white *sodium* salt. p-*Ethylcarbonatobenzaldehyde* (I), prepared from p-hydroxy-benzaldehyde and ethyl chloroformate in the presence of alkali, is a colourless oil, b. p. 170—172°/13 mm., and yields *β-nitro*-p-*ethylcarbonatostyrene* (II), crystallising in slender, pale yellow needles, m. p. 112—113°.

β-Nitro-a-p-ethylcarbonatophenylethyl alcohol (III) forms yellow needles, m. p. 91·5°. *β-Nitro*-p-*hydroxystyrene* (IV), prepared by hydrolysing its acyl derivatives with cold aqueous potassium hydroxide, crystallises in stout, long needles, m. p. 154—160° (decomp.). *β-Nitro-a*-p-*hydroxyphenylethyl alcohol* (V) is a yellow syrup.

4-*Benzoyloxy-3-methoxybenzaldehyde*, prepared by benzoylating vanillin by the pyridine method, has m. p. 75—76°, and condenses with nitro-methane, yielding *β-nitro-4-benzoyloxy-3-methoxystyrene*, which forms slender, pale yellow needles, m. p. 152—155°, and is hydrolysed by alcoholic potassium hydroxide to vanillylidenenitromethane (A., 1905, i, 65).

4-*Ethylcarbonato-3-methoxybenzaldehyde*, prepared from vanillin and ethyl chloroformate, has m. p. 71° and loses CO_2, at 135°, yielding 3-methoxy-4-ethoxybenzaldehyde; with nitromethane it yields *β-nitro-4-ethylcarbonato-3-methoxystyrene*, m. p. 125°, and *β-nitro-a-4-ethylcarbonato-3-methoxyphenylethyl alcohol*, which crystallises in stout needles, m. p. 84—86°.

3 : 4-*Dibenzoyloxybenzaldehyde*, prepared from protocatechualdehyde in a similar manner to that given for p-benzoyloxybenzaldehyde, separates from alcohol in rosettes of white needles, m. p. 96—97°, and gives rise to *β-nitro-3* : 4-*dibenzoyloxystyrene*,

$$C_6H_3(OBz)_2 \cdot CH:CH \cdot NO_2,$$
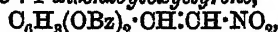
which forms slender, pale yellow needles, m. p. 143—144°, and is hydrolysed by alcoholic potassium hydroxide to *β-nitro-3* : 4-*dihydroxy-styrene*, crystallising in yellow needles or leaflets, m. p. 155—157°, with previous darkening at 145—148° (decomp. 160°).

3 : 4-*Diethylcarbonatobenzaldehyde*, obtained from ethyl chloroformate and protocatechualdehyde, is a colourless oil, b. p. 215—217°/13 mm., and yields with nitromethane, *β-nitro-3* : 4-*diethylcarbonatostyrene*, yellow needles, m. p. 72°.

Acidification of the products, resulting from the condensation of 3 : 4-diethylcarbonato- and 3 : 4-dibenzoyloxy-benzaldehyde with nitro-methane in the presence of sodium methoxide, with acetic acid yields *β-nitro-a-3* : 4-*diethylcarbonatophenylethyl alcohol* and *β-nitro-3* : 4-*dibenzoyloxyphenylethyl alcohol*, as yellow oils. If excess of sodium methoxide is used, *β-nitro-3* : 4-*dihydroxyphenylethyl alcohol* is formed. *Alkyl ethers* of the last-mentioned compound have also been prepared, but these resemble the previously-mentioned nitro-alcohols derived from 3 : 4-dihydroxybenzaldehyde in being too unstable to allow of their isolation in a state of purity. Their constitution was therefore established by reduction to the corresponding amino-alcohols and ethers.

β-Hydroxy-β-phenylethylamine is obtained by reducing *β-nitro-a-*

phenylethyl alcohol with sodium amalgam and acetic acid in aqueous alcoholic solution; it is accompanied by a substance of feeble basic properties, m. p. 217—218°.

β-Methoxy-β-phenylethylamine hydrochloride,

$$OMe \cdot CHPh \cdot CH_2 \cdot NH_2, HCl,$$

obtained by reduction of β-nitro-α-phenylethyl methyl ether in a similar manner, crystallises in white needles, m. p. 158—159°.

Successive treatment of β-nitro-*p*-methoxystyrene with alcoholic potassium hydroxide and acetic acid gives rise to *β-nitro-α-p-methoxyphenylethyl ethyl ether.*. On reduction this yields *β-ethoxy-β-p-methoxyphenylethylamine,* $OMe \cdot C_6H_4 \cdot CH(OEt) \cdot CH_2 \cdot NH_2$, as a syrup which slowly crystallises and yields a hydrochloride, m. p. 173—175° (decomp. 182°).

β-Methoxy-β-p-methoxyphenylethylamine, obtained from β-nitro-α-*p*-methoxyphenylethyl methyl ether, forms a *hydrochloride,* crystallising in white needles, m. p. 166—166·5° (decomp. 186—187°).

β-Hydroxy-β-p-methoxyphenylethylamine hydrochloride has m. p. 171—172°.

β-Nitro-β-3 : 4-dimethoxyphenylethyl methyl ether, obtained as a yellow oil by dissolving β-nitro-3 : 4-dimethoxystyrene (A., 1911, i, 34) in methyl-alcoholic sodium methoxide, is reduced by sodium amalgam and acetic acid to β-methoxy-β-3 : 4-dimethoxyphenylethylamine, identical with the arterenol trimethyl ether of Mannich and Neumann (A., 1910, i, 413).

The condensation of veratraldehyde and nitromethane with sodium methoxide yields the *sodium* salt of *β-nitro-α-3 : 4-dimethoxyphenylethyl alcohol,* which on decomposition with acetic acid and subsequent reduction is converted into *β-hydroxy-β-3 : 4-dimethoxyphenylethylamine,* $C_6H_3(OMe)_2 \cdot CH(OH) \cdot CH_2 \cdot NH_2$, the *hydrochloride* of which crystallises in leaflets, m. p. 163°.

β-Hydroxy-3 : 4-dihydroxyphenylethylamine is obtained in an impure condition by the reduction of β-nitro-α-3 : 4-dihydroxyphenylethyl alcohol; the *hydrochloride* gives an intense catechol reaction with ferric chloride.   F. B.

Action of Sulphuric Acid on Tetramethyldiaminobenzhydrol. The Pinacone of Michler's Ketone. S. FISCHL (*Monatsh.*, 1913, 34, 337—350).—The observation of Rosenstiehl (A., 1895, i, 541) and of Weil (A., 1894, i, 419; 1895, ii, 145), that tetramethyldiaminobenzhydrol is converted into hexamethyltriaminotriphenylmethane by warming with dilute sulphuric acid is confirmed, and it is further shown that by the action of sulphuric acid, Michler's ketone is formed, which then condenses with some of the unchanged hydrol producing a substance of the formula :

$$CH(C_6H_4 \cdot NMe_2)_2 \cdot C_6H_3(NMe_2) \cdot CO \cdot C_6H_4 \cdot NMe_2.$$
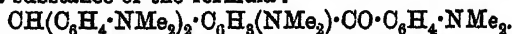
Tetramethyldiaminobenzhydrol, when dissolved in sulphuric acid and gently warmed, furnishes Michler's ketone (tetramethyldiaminobenzophenone), together with a *substance,* $C_{34}H_{40}ON_4$, m. p. 212—213°, crystallising from methyl alcohol in slender, silky needles, or from benzene on addition of light petroleum in short colourless prisms ; it is readily soluble in benzene, less so in acetone, and must have the

constitution given above, since it is also formed by the condensation of Michler's ketone with tetramethyldiaminobenzhydrol in presence of sulphuric acid.   It is unaffected by acids or alkalis, but on oxidation furnishes a greenish-blue dye.   The reactions of the substance indicate that the ·CO· group is in the ortho-position to the methane residue.

Tetramethyldiaminobenzophenone is not affected by zinc and acetic acid, but may be reduced electrolytically or by zinc with sulphuric or hydrochloric acid, giving the corresponding pinacone,

$$OH \cdot C(C_6H_4 \cdot NMe_2)_2 \cdot C(C_6H_4 \cdot NMe_2)_2 \cdot OH,$$
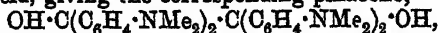
m. p. 195° (compare Escherich and Moest, A., 1903, i, 89).   This is somewhat soluble in benzene, but almost insoluble in alcohol; its solution in acetic acid is colourless in the cold, but becomes blue on warming.   It dissolves in sulphuric acid, forming a deep red solution, which on heating at 115—120° gives rise to the corresponding *pinacolin*,

$$C_{34}H_{40}ON_4,$$
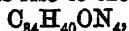
m. p. 232—233°, which crystallises with one mol. of benzene in glandular masses of glancing prisms.   On heating with alcoholic potassium hydroxide, the pinacone is converted into a mixture of the ketone and the hydrol.   T. A. H.

1 : 1-Dimethylol*cyclo*butane.   NICOLAI D. ZELINSKI and M. N. UJEDINOV (*Ber.*, 1913, 46, 1093—1094).—A solution of ethyl tetramethylenedicarboxylate in absolute alcohol was added to sodium covered with dry ether, and, after the first vigorous action had subsided, the product was heated at 130—140° until the sodium was completely dissolved.   After addition of water, the alcohol was removed by distillation and the residue poured into water and saturated with potassium carbonate. The oil which separated was removed, united with a portion obtained by extracting the aqueous liquor with ether, and fractionated.   Thereby, cyclo*butylcarbinol*, $C_4H_7 \cdot CH_2 \cdot OH$, b. p. 142—144°/760 mm., was obtained, together with 1 : 1-*dimethylolcyclobutane*, $C_4H_6(CH_2 \cdot OH)_2$, a viscous, pale yellow oil, b. p. 145—147°/20 mm.   H. W.

The Iodohydrin of the Glycol Derived from Cinnamyl Methyl Ether.   HENRI BEAUFOUR (*Bull. Soc. chim.*, 1913, [iv], 13, 349—353.   Compare A., 1912, i, 621).—The iodohydrin obtained by treating cinnamyl methyl ether with iodine and mercuric oxide (*loc. cit.*) may have the formula $OH \cdot CHPh \cdot CHI \cdot CH_2 \cdot OMe$ or

$$CHPhI \cdot CH(OH) \cdot CH_2 \cdot OMe.$$

The results recorded in this and the next abstract support the first formula.

On treatment with powdered potassium hydroxide the iodohydrin (D$_{10}^{10}$ 1·500) furnishes the corresponding *oxide*, $CHPh \overset{O}{\underset{CH \cdot CH_2 \cdot OMe}{\diagdown}}$,

D$_0^0$ 1·0714, b. p. 127—128°/14 mm., a mobile, colourless liquid with a pungent odour; it does not combine with bromine, but reacts energetically with hydriodic acid, forming an iodo-derivative which probably has the second formula quoted above.

With dimethylamine the iodohydrin yields *ω-methoxymethylephedrine*,

OH·CHPh·CH(NMe$_2$)·CH$_2$·OMe, m. p. 76°, h. p. 152—153°/12 mm., which crystallises in colourless needles, and furnishes a *hydrochloride*, m. p. 170°, *hydriodide* m. p. 102—103°, *methiodide*, m. p. 160°, *picrate*, m. p. 152—153°, and with ethyl chloroacetate a *morpholone*, m. p. 168°. The *hydrochloride* of the *benzoyl* derivative, m. p. 118°, crystallises in spangles, has a bitter taste, and has a slow but distinct numbing action on the tongue. T. A. H.

Alkyliodohydrins Derived from Cinnamyl Methyl Ether. HENRI BEAUFOUR (*Bull. Soc. chim.*, 1913, [iv], 13, 354—358. Compare A., 1912, i, 621, and preceding abstract).—The methyl- and ethyl-iodohydrins, OR·CHPh·CHI·CH$_2$·OMe, already described differ from the simple iodohydrin (preceding abstract) in being more stable. The methyliodohydrin, D$_0^0$ 1·5070, b. p. 160—161°/15 mm., does not react with potassium hydroxide, except in alcohol, and then furnishes at 100°, the *ether*, OMe·CPh:CH·CH$_2$·OMe, D$_0^0$ 1·0483, b. p. 243°/760 mm., 128—129°/13 mm., a strongly-smelling liquid, which combines vigorously with bromine, reduces potassium permanganate solution, and when treated with steam in presence of sulphuric acid yields *phenyl vinyl ketone*, COPh·CH:CH$_2$, b. p. 110—115°/15 mm., which readily polymerises, and yields a *dibromide*, m. p. 56°, crystallising in colourless needles.

The methyliodohydrin reacts only feebly with dimethylamine at 120°, giving the *amine*, OMe·CHPh·CH(NMe$_2$)·CH$_2$·OMe, b. p. 132—133°/11 mm., whilst at higher temperatures, tarry products result.

The ethyliodohydrin (D$_0^0$ 1·4568) behaves like its lower homologue, and with potassium hydroxide in alcohol yields the ethylenic *ether*, OEt·CPh:CH·CH$_2$·OMe, D$_0^0$ 1·0428, b. p. 137—139°/15 mm., whilst with dimethylamine it is even less reactive. T. A. H.

Preparation of Aromatic Amino-alcohols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 256750).—The previously described reduction of amino-ketones in the presence of colloidal metals of the platinum group (this vol., i, 361) is found to proceed equally satisfactorily if the metal is in a state of very fine division, and the preparation of 3 : 4-dihydroxyphenyl-α-propanolamine and of 3 : 4-dimethoxyphenyl-α-propanolamine in the presence of finely-divided palladous chloride are described. F. M. G. M.

1 - Methyl*cyclo*pentane - 1 - carboxylic Acid. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 184—188).—*cyclo*Pentanone (compare Aschan, A., 1912, i, 536) was converted into 1-methyl*cyclo*pentan-1-ol (compare Zelinski and Nametkin, A., 1902, i, 672), this into 1-methyl-1-chloro*cyclo*pentane, and the latter, by the action of magnesium in ethereal solution and then of carbon dioxide, into 1 - *methylcyclopentane* - 1 - *carboxylic acid*, $\genfrac{}{}{0pt}{}{CH_2·CH_2}{CH_2·CH_2}$>CMe·CO$_2$H, which is an unpleasant smelling liquid, b. p. 219—219·5°, D$_4^{10}$ 1·0218, D$_4^0$ 1·0392. Its *silver* and *cadmium* salts were analysed. The *methyl* ester, C$_8$H$_{14}$O$_2$, b. p. 159·5°/721 mm., D$_4^{20}$ 0·9641, D$_4^0$ 0·9850, D$_4^{185}$ 0·9657, n_D^{185} 1·43727, and the *amide*, C$_7$H$_{13}$ON, m. p. 124—125° were prepared. T. H. P.

Dihydrocamphoceic Acid (Camphenilolic Acid) and the Action of Sodium on Camphenilone. S. V. Hintikka (*Chem. Zentr.*, 1913, i, 625 ; from *Ann. Acad. Sci. Fennicae*, 1913, **9**, 1—7). —*Camphenilolic acid*, $C_{18}H_{15}\cdot CO_2H$, is obtained by heating camphenilone with powdered potassium hydroxide, as an oil, b. p. 140—141°/15 mm., D_4^{20} 0·9820, n_D 1·45650. It forms a *chloride*, b. p. 112—114°/10 mm., a *methyl* ester, mobile oil, b. p. 203—204°/762 mm., D_4^{21} 0·9392, n_D 1·44441, and an *anilide*, $C_8H_{15}\cdot CO\cdot NHPh$, in radiating needles, m. p. 89—90°. If the acid had Wallach's formula (I) it should give a hydroxy-acid on oxidation, which should further yield the lactone, dimethylnorcampholide. It undergoes extensive decomposition, however, and the products include acetic acid and probably butyric acid.

$$\begin{array}{ccc}
\mathrm{CH_2\cdot CH\cdot CHMe_2} & \mathrm{CH_2\!-\!\!-CH_2} & \mathrm{CH_2\!-\!CH_2} \\
|\quad\ \mathrm{CH_2} & \mathrm{CH\cdot CH_2\cdot C\!-\!\!-\!\!-C\cdot CH_2\cdot CH} & \\
\mathrm{CH_2\cdot CH\cdot CO_2H} & \mathrm{CMe_2\!-\!\!-CH\cdot OH\ \ CO\!-\!\!-CMe_2} & \\
\text{(I.)} & \text{(II.)} &
\end{array}$$
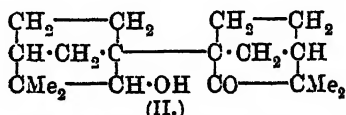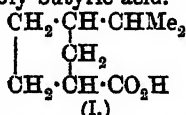
When boiled with sodium in xylene, camphenilone yields a yellow, viscous *oil*, $C_{18}H_{28}O_2$ (II?), b. p. 172—174°/12 mm., D_4^{20} 1·0601, n_D 1·51547.   J. C. W.

Direct Hydrogenation of the Hydrocinnamic Esters: Preparation of β-*cyclo*Hexylpropionic Acid. Paul Sabatier and Marcel Murat (*Compt. rend.*, 1913, **156**, 751—753).—The esters of β-phenylpropionic acid like those of phenylacetic acid (compare this vol., i, 362) readily undergo direct hydrogenation in the presence of active nickel at 170—185°, giving the corresponding esters of β-*cyclo*hexylpropionic acid in a pure state. The following have been prepared :

Methyl β-cyclohexylpropionate, b. p. 222—224° (corr.), D_0^0 0·9705, D_0^{16} 0·9603, n_D^{16} 1·453.

Ethyl β-cyclohexylpropionate, b. p. 231° (corr.), D_0^0 0·9512, D_0^{17} 0·9383, n_D^{17} 1·452.

Propyl β-cyclohexylpropionate, b. p. 251—252° (corr.), D_0^0 0·9467, D_0^{15} 0·9322, n_D^{15} 1·455.

iso*Butyl* β-cyclohexylpropionate, b. p. 260° (corr.), D_0^0 0·9368, D_0^{15} 0·9281, n_D^{16} 1·456.

Whilst the densities decrease with increase in molecular weight the refractive indices remain practically constant. All these esters are readily saponified by warming with alcoholic potassium hydroxide, and with dilute sulphuric acid yield β-*cyclo*hexylpropionic acid (compare Ipatiev, A., 1909, i, 472).   W. G.

Influence of the Nature and Position of Substituents on the Stability of the Carboxyl Group in Substituted Benzoic Acids. Franz von Hemmelmayr (*Monatsh.*, 1913, **34**, 365—388. Compare Cazeneuve, A., 1895, i, 57).—The relative stability of the carboxyl group in various substituted benzoic acids was determined by boiling the acids in solution in water or aniline and estimating the proportion decomposed in a certain time. The results, which are tabulated in detail and fully discussed, show that it is difficult to draw general conclusions as to the influence of the position of substituents on the stability of the carboxyl group. The four substituents

investigated are arranged in the following descending order as regards their effect on the stability of the carboxyl group : ·OH, ·NO₂, ·Br, ·NH₂. T. A. H.

Preparation of Nuclear Nitroso-derivatives of Phenyl-glycine-o-carboxylic Acids, their Acids and Neutral Esters. J. D. RIEDEL (D.R.-P. 256461. Compare A., 1887, 729, 1114; 1909, i, 794, 645).—When a cold concentrated hydrochloric acid solution of phenylglycine-o-carboxylic acid (5 parts) is treated with sodium nitrite, it furnishes p-*nitrosophenylglycine-o-carboxylic acid hydrochloride*, decomp. about 100°; the free *base*, a green powder, condenses with p-nitrobenzonitrile to furnish an *azomethine*, red needles, m. p. 256—258°, and with benzonitrile to give a yellow *compound*.

Dimethyl p-*nitrosophenylglycine*-o-*carboxylate* has m. p. 164—165°, and the *diethyl* ester, m. p. 131°.

p-*Nitroso-o-carbomethoxyphenylglycine ethyl* ester is a green, crystalline compound, m. p. 125°, and p *nitroso-o-carboxyphenylglycine ethyl* ester has m. p. 115—116°. F. M. G. M.

Preparation of Derivatives of Arylalkyloxyacetic Acids. GESELLSCHAFT FUR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 256756. Compare McKenzie, T., 1899, 75, 755).—a-*Ethoxy-a-phenylacetamide*, OEt·CHPh·CO·NH₂, colourless needles, m. p. 90°, is obtained when ethyl ethoxyphenylacetate, b. p. 145—147°/20 mm., is shaken with saturated ammonium hydroxide; the following derivatives have been obtained in an analogous manner.

a-*Methoxyphenylacetamide*, m. p. 110—111°, from *ethyl* a-*methoxy-phenylacetate*, b. p. 148—152°/22 mm.

p-*Tolyloxyethylacetamide*, m. p. 130—131°, from *ethyl* p-*tolyloxyethyl-acetic acid*, b. p. 160—165°/25 mm.

o-*Chlorophenoxyallylacetamide*, a colourless oil, b. p. 171—174°/21 mm., from *ethyl* o-*chlorophenoxyallylacetate*, b. p. 166—170°/25 mm.

Phenoxyallylacetamide, m. p. 77—78°, from *ethyl phenoxyallylacetate*, b. p. 163—164°/24 mm.

Phenoxyphenylacetamide, OPh·CHPh·CO·NH₂, colourless needles, m. p. 154—155°, from phenoxyphenylacetic acid; the *carbamide*,

$$OPh·CHPh·CO·NH·CO·NH_2,$$

colourless needles, has m. p. 193°. F. M. G. M.

Stereoisomeric *iso*Fenchocamphoric Acids. A. E. SANDELIN (*Annalen*, 1913, 396, 285—335).—The constitution,

$$\begin{array}{l}CMe_2·CH(CO_2H)\\CH_2·OMe(CO_2H)\end{array}\!\!>CH_2,$$
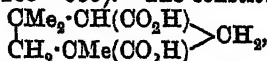
of *iso*fenchocamphoric acid has been proved by Aschan. Theoretically, six stereoisomerides are possible, four active and two racemic. Wallach has prepared the *cis-d-* and *l*-acids, and has shown that by mixture they produce the *cis-dl*-acid, which has been obtained by Aschan. The latter has also shown that the *cis-dl*-acid is partly changed to the *trans-dl*-acid by warming with glacial acetic and hydrochloric acids. The *trans-d-* and *l*-acids hitherto have been unknown, but have now been prepared by the author. A large

number of derivatives of all the acids have also been prepared for comparative purposes. The two active *cis*-acids behave alike chemically and physically, except in the sign of the rotation ; the same is true of the active *trans*-acids. The fact that the *cis*-acid can be changed to the *trans*-acid, and vice versa proves that the two are geometrical isomerides.

trans-d- and l-iso*Fenchocamphoric acids* are prepared by heating the corresponding *cis*-acids for twenty-four hours at 180—200° with a mixture of equal parts of glacial acetic acid and hydrochloric acid, D 1·20. The product, which consists of approximately equal quantities of the *trans*- and the *cis*-acids (the same product is obtained by treating the pure *trans*-acid in the same manner), is treated with acetyl chloride, and the resulting mixture of *cis*-anhydride and *trans*-acid is extracted in a Soxhlet apparatus with carbon tetrachloride, in which the *trans*-acid is insoluble. Another method of partly changing the *cis*- to the *trans*-acid is the hydrolysis of the acid chloride.

cis-d- and l-iso*Fenchocamphoric acids* crystallise in prisms, have m. p. 158—159°, K 0·00492, $[a]_D^{20}$ + 14·58° and − 14·54° respectively in alcohol, and solubility (that is, amount dissolved by 100 grams of water at 25°) 1·409 and 1·412 grams respectively ; *cis-dl-iso*fenchocamphoric acid crystallises in leaflets, and has m. p. 174—175°, K 0·00491, and solubility 0·224. *trans-d-* and l-iso*Fenchocamphoric acids* crystallise in prisms, and have m. p. 149—150·5°, K 0·00419 and 0·00421 respectively, $[a]_D^{20}$ + 4·19° and − 4·16° respectively, and solubility 0·460 and 0·458 respectively ; *trans-dl-iso*fenchocamphoric acid crystallises in leaflets, and has m. p. 173—174°, K 0 00420, and solubility 0·180.

cis-d- and l-iso*Fenchocamphoric anhydrides* crystallise in prisms, and have m. p. 98° and $[a]_D^{20}$ + 13·33° and − 13·46° respectively in benzene ; *cis-dl-iso*fenchocamphoric anhydride has m. p. 95—96°. These anhydrides are easily hydrolysed by water.

All the *iso*fenchocamphoric acids are readily esterified by the necessary alcohol and sulphuric acid, and yield, contrary to expectation, mainly the normal esters. *Methyl* cis-d-iso*fenchocamphorate* has b. p. 253—255°/764 mm., D_4^{20} 1·0484, n_D^{19} 1·45166, and $[a]_D^{15}$ + 19·17° ; the *l-ester* has b. p. 253—255°/780 mm., D_4^{20} 1·0470, n_D^{12} 1·45388°, and $[a]_D^{12}$ − 19·06°. *Methyl* cis-dl-iso*fenchocamphorate* has b. p. 252—253°/760 mm., D_4^{20} 1·0490, n_D^{20} 1·45206. *Methyl* trans-d-iso*fenchocamphorate* has b. p. 248—249°/757 mm., D_4^{20} 1·0467, n_D^{15} 1·45267, $[a]_D^{15}$ − 1·14° ; the l-*ester* has the same b. p., D_4^{20} 1·0471, n_D^{16} 1·45186, $[a]_D^{15}$ + 1·18. *Methyl* trans-dl-iso*fenchocamphorate* has b. p. 247—248°/757 mm., D_4^{20} 1·0448, $n_D^{15·5}$ 1·45176. *Ethyl* cis-d-iso*fenchocamphorate* has b. p. 269—271°/764 mm., D_4^{20} 1·0067, n_D^{20} 1·44656, $[a]_D^{20}$ + 11·52° ; the l-*ester* has b. p. 270—272°/780 mm., D_4^{20} 1·0073°, n_D^{12} 1·44926, and $[a]_D^{12}$ − 11·16°. *Ethyl* trans-d-iso*fenchocamphorate* has b. p. 266—267°/750 mm., D_4^{20} 1·0057, n_D^{16} 1·44656, $[a]_D^{15}$ − 1·05° ; the l-*ester* has the same b. p., D_4^{20} 1·0053, n_D^{20} 1·44646, and $[a]_D^{15}$ + 0·99°. *Ethyl* trans-dl-iso*fenchocamphorate* has b. p. 264—265°/750 mm., D_4^{20} 1·0035, n_D^{15} 1·44576.

a-Alkyl hydrogen *iso*fenchocamphorates, $\begin{matrix} CMe_2 \cdot CH(CO_2R) \\ CH_2 \cdot CMe(CO_2H) \end{matrix} > CH_2$, are obtained as by-products in the esterification of the acids, and also by

the action of sodium alkyloxides on the anhydrides; β-alkyl hydrogen esters are produced by the partial hydrolysis of the normal esters. These hydrogen esters are, almost without exception, viscous liquids which have not been obtained in a pure state. The dianilides of the *iso*fenchocamphoric acids are obtained from the acid chlorides and aniline in cold ether. cis-d- and l-iso*Fenchocamphordianilides* have m. p. 184—185°, and $[a]_D^{18}$ + 26·26° and − 26·53° respectively in alcohol, and the dl *anilide* has m. p. 142—144°. trans-d- and l-iso*Fenchocamphoranilides* have m. p. 190—191° and $[a]_D$ − 20·30° and + 20·69° respectively in alcohol, whilst the dl-*anilide* has m. p. 185—187°. It is noteworthy that the replacement of the two chlorine atoms of the acid chloride by the anilino-group yields only one of the two possible, geometrically isomeric dianilides, whereas their replacement by hydroxyl gives both *cis-* and *trans-iso*fenchocamphoric acids.

Diamides of the *cis*-acids cannot be prepared. By passing dry ammonia into a cold solution of the respective acid chlorides in ethyl acetate, trans-d- and l-iso*fenchocamphordiamides*, $C_{10}H_{18}O_2N_2,H_2O$, m. p. 95—96° and 95—97° respectively, $[a]_D^{17}$ − 6·18° and + 6·37° respectively in alcohol, and trans-dl-iso*fenchocamphordiamide*, $C_{10}H_{18}O_2N_2$, m. p. 202—204°, are obtained. cis-d- and l-iso*Fenchocamphorimides*, m. p. 120—121°, $[a]_D^{18}$ − 12·73° and + 12·67° respectively in alcohol, and the dl-*imide*, m. p. 122—123°, are obtained by heating the ammonium salts of the corresponding acids at 180—200° for twenty-four hours.

a-cis l-iso-*Fenchocamphoramic acid*, $\dfrac{CMe_2 \cdot CH(CO \cdot NH_2)}{CH_2 \!-\! CMe(CO_2H)} \!\!>\!\! CH_2$, is pre-
pared best by treating a cold ethereal solution of the *cis-l*-anhydride with dry ammonia and treating the concentrated aqueous solution of the product with hydrochloric acid. It has m. p. 220° (decomp.), decomposes when heated slowly, has $[a]_D^{20}$ − 11·18° in alcohol, and yields *cis-l-iso*fenchocamphoric anhydride above its m. p. a-cis-d-iso*Fenchocamphoramic acid*, m. p. 220° (decomp), $[a]_D^{20}$ + 10·99° in alcohol, and the a-cis-dl *isomeride*, m. p. 208° (decomp.), are prepared by similar methods. a-trans-d-, l-, and dl-iso*Fenchocamphoramic acids*, m. p. 210—211°, 210—211°, and 205° respectively, are obtained as by-products in the preparation of the diamides; the active acids have $[a]_D^{18}$ + 7·98° and − 7·94° respectively in alcohol.

β-cis-d- and l-iso*Fenchocamphoramic acids*, $\dfrac{CMe_2 \!-\! CH(CO_2H)}{CH_2 \cdot CMe(CO \cdot NH_2)} \!\!>\!\! CH_2$,
m. p. 180—181°, $[a]_D^{18}$ + 8·91° and − 8·75° respectively in alcohol, and the cis-dl-*isomeride*, m. p. 194—195°, are prepared by boiling the respective imides with aqueous sodium hydroxide for two hours and acidifying. The yield is quantitative, and the acids are only very slowly attacked by boiling water, crystallising therefrom in well-formed needles. β-trans-d- and l-iso*Fenchocamphoramic acids*, m. p. 179—180°, $[a]_D^{17}$ + 9·71° and − 9·57° respectively in alcohol, and the dl-*isomeride*, m. p. 155—156° (when crystallised from chloroform, the substance forms needles containing $CHCl_3$, m. p. 151—152°), are prepared by acidifying the solution obtained by boiling the respective diamides with the calculated amount of aqueous sodium hydroxide.　　　　C. S.
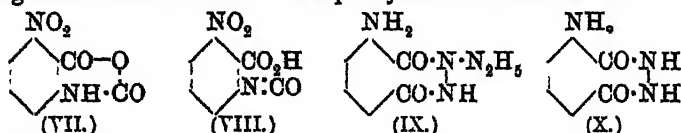
Behaviour of the 1-Ester of 3-Nitrophthalic Acid Towards Hydrazine. THEODOR CURTIUS and AUGUST SEMPER (*Ber.*, 1913, **46**, 1162—1171).—Miller's monoethyl 3-nitrophthalate (I) (A., 1882, 404), the constitution of which is ascertained in the present researches, has been converted into the hydrazine salt of *o*-nitrophthalic monohydrazide (II), and this into the acid hydrazide (III), and finally into the azoimide (IV).

$$
\begin{array}{cccc}
\text{NO}_2 & \text{NO}_2 & \text{NO}_2 & \text{NO}_2 \\
\text{CO}_2\text{H} & \text{CO}_2\text{N}_2\text{H}_5 & \text{CO}_2\text{H} & \text{CO}_2\text{H} \\
\text{CO}_2\text{Et} & \text{CO·NH·NH}_2 & \text{CO·NH·NH}_2 & \text{CO·N}_3 \\
\text{(I.)} & \text{(II.)} & \text{(III)} & \text{(IV.)}
\end{array}
$$
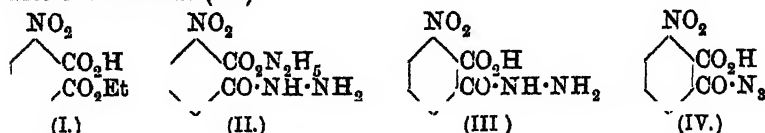
The latter substance loses hydrazoic acid when boiled with water or alcohol, forming *o*-nitrophthalic acid with water and the acid-ester (V) with alcohol. This isomeric acid-ester only gives a hydrazine salt with hydrazine, and, unlike the starting material, it is easily converted into the diethyl ester.

$$
\begin{array}{cc}
\text{NO}_2 & \text{NO}_2 \\
\text{CO}_2\text{Et} & \text{CO}_2\text{Et} \\
\text{CO}_2\text{H} & \text{CO}_2\text{·N}_2\text{H}_5 \\
\text{(V.)} & \text{(VI.)}
\end{array}
$$
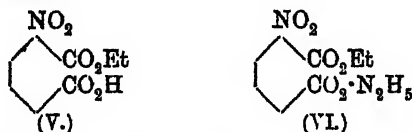
When the acid-azoimide is heated in benzene or chloroform, however, it slowly loses nitrogen and yields *o*-nitroisatoic anhydride (VII). The carbimide (VIII) might have been expected, but the substance gives, on boiling with water, not a carbamide, but 6-nitro-2-aminobenzoic acid, forms a urethane only on prolonged boiling with alcohol, and gives a benzanilide and not a phenylcarbamide with aniline.

$$
\begin{array}{cccc}
\text{NO}_2 & \text{NO}_2 & \text{NH}_2 & \text{NH}_2 \\
\text{CO—O} & \text{CO}_2\text{H} & \text{CO·N·N}_2\text{H}_5 & \text{CO·NH} \\
\text{NH·CO} & \text{N:CO} & \text{CO·NH} & \text{CO·NH} \\
\text{(VII.)} & \text{(VIII.)} & \text{(IX.)} & \text{(X.)}
\end{array}
$$

When heated with dilute sulphuric acid, the substance is also deprived of the carboxyl group and converted into *m*-nitroaniline.

If the initial acid-ester be boiled with an excess of hydrazine hydrate, the nitro-group is reduced, and water eliminated from the hydrazine salt of the monohydrazide, with the formation of the hydrazi-compound (IX), which is resolved into the aminohydrazide (X) by water. This compound was also obtained from triethyl *hemi*mellitate (Schmitz, *Diss.*, Heidelberg, 1902) according to the scheme:

$$
\begin{array}{ccccc}
\text{CO}_2\text{Et} & & \text{CO·NH·NH}_2 & & \text{CO·N}_3 \\
\text{CO}_2\text{Et} & \xrightarrow{\text{N}_2\text{H}_4} & \text{CO·NH} & \xrightarrow{\text{HNO}_2} & \text{CO·NH} \\
\text{CO}_2\text{Et} & & \text{CO·NH} & & \text{CO·NH} \\
\end{array}
$$

$$
\begin{array}{cc}
& \text{NH·CO}_2\text{Et} & & \text{NH}_2 \\
\xrightarrow{\text{C}_2\text{H}_5\text{OH}} & \text{CO·NH} & & \text{CO·NH} \\
& \text{CO·NH} & & \text{CO·NH}
\end{array}
$$
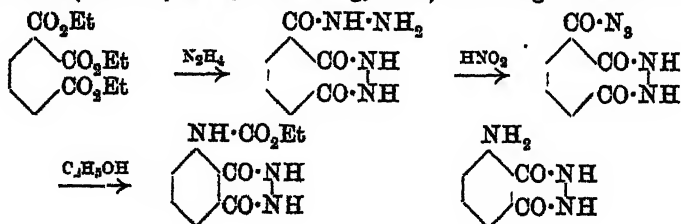
For the preparation of the *hydrazine* salt of *o-nitrophthalic acid monohydrazide* (II), Miller's ester, m. p. 110°, is triturated with hydrazine hydrate. It forms colourless needles, m. p. 157°, which yield the *benzylidene* compound of the acid-hydrazide,

$$CO_2H \cdot C_6H_3(NO_2) \cdot CO \cdot NH \cdot N\!:\!CHPh,$$
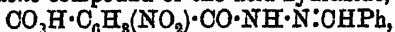
in small, colourless needles, m. p. 177°, and, with hydrochloric acid, the *acid hydrazide* (III), in flat needles, m. p. above 280°, from which the *azoimide* (IV) is obtained in colourless, shimmering scales by the addition of sodium nitrite to the suspension in concentrated hydrochloric acid. After prolonged boiling with absolute alcohol the azoimide is converted into the *acid-ester* (V), which forms yellow needles, m. p. 157°, but when heated in dry chloroform the product is *o-nitroisatoic anhydride* (VII), which crystallises in pale yellow, flat needles, m. p. 215°, and is isomeric with Kolbe's nitroisatoic anhydride (A., 1885, i, 666), which gave 5-nitro-2-aminobenzoic acid on boiling with water. It gradually dissolves in boiling absolute alcohol, forming the *urethane*, $C_{10}H_{10}O_6N_2$, in faintly yellow, flat needles, m. p. 187°, which yield *m*-nitroaniline with dilute acids. It also forms the *anilide*, $C_{15}H_{11}O_3N_3$, in slender, yellow needles, m. p. 137°.

The *hydrazine* salt of the cyclic *hydrazide* of *o-aminophthalic acid* (IX) results when the starting material is heated with an excess of hydrazine hydrate. The free *hydrazide* (X) is a yellow solid, which behaves as a monobasic acid, forming *barium*, *potassium*, and *sodium* salts. It is also soluble in dilute acids, and gives a blue fluorescence in hot glacial acetic acid (compare Schmitz, *loc. cit.*).

<div align="right">J. C. W.</div>

Preparation of *αβ*-Diketonic Esters. ANDRÉ WAHL and M. DOLL (*Bull. Soc. chim.*, 1913, [iv], 13, 332—348. Compare A., 1904, i, 556; 1907, i, 217; 1911, i, 108; 1912, i, 536, 625).—This paper discusses in detail the mechanism of the reaction between "nitrous fumes" and acylacetic esters, by means of which the methylene group of the latter is converted into a carbonyl group, with the formation of *αβ*-diketonic esters. Examples of this reaction have been recorded already (*loc. cit.*). The reaction occurs in two stages: (1) the formation of an oximino-derivative of the acylacetate (A., 1904, i, 556; 1905, i, 409), and (2) the conversion of this oximino-derivative into the corresponding *αβ*-diketonic ester by the action of "nitrous fumes." The latter were obtained by treating "chamber crystals" with sodium nitrite, and as applied consisted chiefly of N_2O_3 and NO_2 (89·2%) with some NO (10%). The gas resulting from the second phase of the reaction was chiefly N_2 (54%), $N_2O_3 + NO_2$ (29%), N_2O (10%), and NO (7%), so that this phase is not unilateral. The following new compounds were prepared.

Methyl benzoylglyoxylate, D_0^0 1·233, b. p. 146—149°/12 mm., is a mobile, orange-yellow liquid, which reduces Fehling's solution and ammoniacal silver nitrate, and yields a *hydrate*, $COPh \cdot CO \cdot CO_2Me, H_2O$, m. p. 65°, crystallising in stellate groups of pearly needles. *Propyl benzoylglyoxylate*, b. p. 155—158°/12 mm., D_0^0 1·159, combines with alcohol or water, but the products are not crystalline. iso*Butyl*

benzoylglyoxylate, D_0^0 1·124, b. p. 161—164°/12 mm., yields a crystalline *monohydrate*, m. p 62—63°.

Ethyl valeroylglyoxylate, b. p. 100—125°/15 mm., was not obtained pure.   T. A. H.

Synthesis of Orsellinic Acid and Everninic Acid. KURT HOESCH (*Ber.*, 1913, 46, 886—892).—Attempts to synthesise orsellinic acid from orcinol by a process analogous to the salicylic acid synthesis yielded only the isomeric *p*-orsellinic acid. The synthesis could, however, be successfully effected by the oxidation of orcylaldehyde.

Orcylaldehyde, obtained from orcinol by the method of Gattermann (A., 1908, i, 28), was found to undergo oxidation more smoothly after converting the hydroxyl groups into methylcarbonato-groups (compare Fischer and Freudenberg, A., 1910, i, 265) by the action of methyl chlorocarbonate and· sodium hydroxide. *Dimethylcarbonato-orcylaldehyde*, $CHO \cdot C_6H_2Me \cdot (O \cdot CO_2Me)_2$, crystallises in needles, m. p. 84—85°, which turn yellow on exposure to light; *methylcarbonato-orcylaldehyde*, $CHO \cdot C_6H_2Me(OH) \cdot O \cdot CO_2Me$, obtained by the action of less methyl chlorocarbonate forms prisms, m. p. 79°. *Diethylcarbonato-orcylaldehyde*, needles, m. p. 60°, obtained analogously to the corresponding dimethylcarbonato-compound, behaves similarly to the latter towards oxidation; when treated in acetone solution at 40° with potassium permanganate, they are oxidised to dimethylcarbonato-orsellinic acid (compare Fischer and Hoesch, A., 1912, i, 859) and *diethylcarbonato-orsellinic acid*, prisms, m. p. 112° (decomp.) respectively. These acids are hydrolysed by *N*-sodium hydroxide solution at room temperature, giving satisfactory yields of orsellinic acid,

$$C_6H_2Me(OH)_2 \cdot CO_2H.$$

If orcylaldehyde is cautiously methylated by methyl sulphate and 2*N*-sodium hydroxide in acetone solution, *everninaldehyde* (2-hydroxy-4-methoxy-6-methylbenzaldehyde) is obtained as needles, m. p. 65°. When heated with anhydrous sodium acetate and acetic anhydride in a sealed tube for five hours at 170—180°, everninaldehyde is converted

into *7-methoxy-5-methyl-1 : 2-benzopyrone*, $OMe \cdot C_6H_2Me \Big\langle \begin{smallmatrix} CH=CH \\ O——CO' \end{smallmatrix}$

long needles, m. p. 146°, which dissolve in concentrated sulphuric acid, giving a blue fluorescence; the success of this synthesis confirms the structure already assumed for everninaldehyde (Fischer and Hoesch, *loc. cit.*). When an acetone solution of everninaldehyde is carefully treated with methyl chlorocarbonate and sodium hydroxide, *methylcarbonatoeverninaldehyde*, $OMe \cdot C_6H_2Me(O \cdot CO_2Me) \cdot CHO$, needles, m. p. 77°, which redden in the light and are phototropic, is obtained. This is oxidisable by potassium permanganate with care to methylcarbonato-everninic acid, silky needles, which decompose near 100°, and can be hydrolysed by *N*-sodium hydroxide at the ordinary temperature to everninic acid, $OMe \cdot C_6H_2Me(OH) \cdot CO_2H$.   D. F. T.

Hydrogenation of Santonin. HEINRICH WIENHAUS and WOLFGANG FELIX VON OETTINGEN (*Annalen*, 1913, 397, 219—246).— By reduction by the Paal-Amberger method, santonin absorbs four atomic proportions of hydrogen, and yields two stereoisomeric tetra-

hydrosantonins. Hence the formulæ of Cannizzaro and Andreocci and of Angeli and Marino, which contain only one ethylenic linking, are disproved. The formulæ of Cannizzaro and Gucci and of Francesconi and Cusmano (A., 1908, i, 272) are permissible, and of the two, the

former, $\begin{matrix} \text{CH}_2 \cdot \text{CMe} \vdots \text{C} \cdot \text{CH}_2 \cdot \text{CH} \text{-----O} \\ \text{CO} \cdot \text{CMe} = \text{C} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CHMe} \end{matrix} \Big\rangle \text{CO}$, is preferable.

When the hydrogenation of santonin is discontinued after 1 mol. of hydrogen has been absorbed, it is found, in accord with Paal's experience with substances containing a conjugated system (A., 1912, i, 703), that the addition does not occur in the sense of Thiele's theory; in other words, one half of the santonin is completely reduced, the other half is unattacked.

Santonin is so readily reduced that 50 grams in methyl alcohol, in the presence of 1 gram of palladous chloride, absorbed 10 litres (at 15° and 745 mm.) of hydrogen in ten minutes; the reduction proceeds even with flocculent (non-colloidal) palladium. The products are α- and β-tetrahydrosantonins, the separation of which is effected by taking advantage of the very slight tendency of β-tetrahydrosantonic acid (see below) to lactone-formation.

α-*Tetrahydrosantonin*, $C_{15}H_{22}O_3$, m. p. 158°, colourless, rectangular leaflets, does not become yellow in light, is unchanged by the action of zinc-dust and warm acetic acid, and forms an *oxime*, m, p. 235—237°, and *semicarbazone*, m.p. 256—258° (decomp.). β-*Tetrahydrosantonin*, $C_{15}H_{22}O_3$, m. p. 105°, stout plates, forms an *oxime*, m. p. 182°, and *semicarbazone*, m. p. 248—250° (decomp.).

During the reduction of anhydrous santoninoxime by the Paal-Amberger method, the oximino-group is attacked, since ammonia and α-tetrahydrosantonin have been isolated from the products. The reduction of aqueous sodium santonate in a similar manner yields α-*tetrahydrosantonic acid*, $C_{15}H_{24}O_4, H_2O$, m. p. 115° (decomp.) (anhydrous, 135—145°), rhombohedral crystals (*sodium* salt, colourless needles or leaflets), and β-*tetrahydrosantonic acid*, $C_{15}H_{24}O_4$, m. p. 200° (decomp.), or 192° slowly heated, colourless plates, which form an *oxime*, $C_{15}H_{25}O_4N$, m. p. 218—220°.

By warming with aqueous sodium hydroxide or carbonate and then acidifying, α-tetrahydrosantonin is converted into α-tetrahydrosantonic acid, which is readily changed back to the lactone by heating, or by keeping its ethereal solution. In a similar manner, β-tetrahydrosantonin is converted into β-tetrahydrosantonic acid. This acid is more stable than the α-isomeride, but is re-converted into β-tetrahydrosantonin by heating at 200° under reduced pressure.

Attempts to convert α-tetrahydrosantonin or the acid into the corresponding β-compounds, and vice versa, have been unsuccessful.

Whilst santonin itself has $[\alpha]_D^{15}$ − 171·70° in methyl alcohol, α-tetrahydrosantonin has a mean value + 17·1° ($[\alpha]_D$ of the oxime in chloroform increases from − 38·05° to − 53·07° with increase of the concentration from 1·63% to 3·34%); β-tetrahydrosantonin has $[\alpha]_D + 41·08°$ when prepared directly from santonin and 9·27° when obtained from the β-acid; α-tetrahydrosantonic acid has $[\alpha]_D + 20·00°$, and the β-acid has $[\alpha]_D + 2·18°$ (both prepared from the sodium salts). C. S.

Santonin. XI. Tetrahydrosantonin. EDGAR WEDEKIND and
E. BENIERS (*Annalen*, 1913, **397**, 246—254. Compare A., 1908, i,
183).—Many of the authors' results are identical with those obtained
by Wienhaus and von Oettingen (preceding abstract). However, by
the reduction of santonin in acetone by hydrogen ($1\frac{1}{4}$ atmospheres) in
the presence of palladous chloride and gum arabic, they have been
unable to isolate β-tetrahydrosantonin. The m. p. of a-tetrahydro-
santoninoxime is given as 219—220°, and that of the *phenylhydrazone*
as 205° (decomp.). a-Tetrahydrosantonin and nitric acid, D 1·4, yield
a-*dinitrotetrahydrosantonin*, $C_{15}H_{20}O_7N_2$, decomp. 187°, large, colourless
plates, $[a]_D + 105\cdot05°$ in alcohol and 90·22° in chloroform.

By bromination in chloroform at 35—40°, a-tetrahydrosantonin
yields a-*bromotetrahydrosantonin*, $C_{15}H_{21}O_8Br$, decomp. 147°, colourless,
prismatic needles, $[a]_D + 9\cdot09°$ in chloroform.   C. S.

Preparation of 1-Aminoanthraquinone-2-carboxylic Acids
and their Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P.
256344. Compare A., 1912, i, 979).—*Ethyl* 1-op-*aichloroanilino-
anthraquinone-2-carboxylate*, coppery-red needles, is obtained when
ethyl 1-*chloroanthraquinone-2-carboxylate* (yellow leaflets, m. p. 142°)
is boiled for five to six hours with *op*-dichloroaniline in nitro-
benzene solution in the presence of cuprous chloride and sodium
acetate ; the free *acid* obtained by its hydrolysis (alcoholic potassium
hydroxide) is a scarlet-red powder. *Methyl* 1-*chloroanthraquinone-2-
carboxylate*, m. p. 164°, can also be employed in this reaction. *Ethyl*
1 : 1'-*anthraquinonylaminoanthraquinone-2-carboxylate* forms scarlet-red
needles and the free *acid* a violet powder, whilst the isomeric *com-
pounds* from ethyl 1-chloroanthraquinone-2-carboxylate with 2-amino-
anthraquinone consist of orange-yellow leaflets and a red powder
respectively. The *compound* from 1-amino-4-hydroxyanthraquinone
and ethyl 1-chloroanthraquinone-2-carboxylate forms violet-blue
needles.

Ethyl 1-*nitroanthraquinone-2-carboxylate*, yellow leaflets, m. p.
232—233°, when condensed with *op*-dichloroaniline gives rise to a
compound, dark red needles ; the free *acid* is a red powder.
                                                      F. M. G. M.

Esters of Polycinnamic Acid. CARL LIEBERMANN and M.
KARDOS (*Ber.*, 1913, **46**, 1055—1066).—In continuation of previous
work (A., 1911, i, 370) on the polymerisation of esters of cinnamic
acid, the authors have investigated the two allyl polycinnamates
described by Seeligmann (*Diss.*, Karlsruhe, 1906). These two esters,
which are termed allyl polycinnamate *A* and *B*, are formed by heating
allyl cinnamate in sealed tubes at 210°.

The ester *A* is obtained by heating for six hours, and isolated from
the resulting liquid by dissolving in benzene and precipitating with a
mixture of alcohol and ether. It separates in heavy, white flocks,
sintering at 190—200°, but possesses no definite m. p.

The ester *B* is best prepared by heating allyl cinnamate for fifteen
hours and extracting the product with benzene, when it is obtained
as a white powder, which becomes brown and decomposes at about

300°; it differs from the ester *A* in being insoluble in benzene and chloroform.

The two polymerides are hydrolysed by boiling with 25% alcoholic potassium hydroxide, but the amount of allyl alcohol produced is only 10—12% of that to be expected on the assumption that the polymerides are allyl esters of polycinnamic acid $(C_9H_8O_2)_x$. The conclusion is therefore drawn that the double linking of the allyl groups takes part in the polymerisation after the manner indicated in the following formula:
$$\begin{array}{c} CH_2 \cdot CHMe \cdot CPh \cdot CH \cdot CO_2 \cdot C_3H_5 \\ | \\ O - CO - CH - CHPh \end{array}.$$

This view is also confirmed by the behaviour of the ester *A* towards bromine. It combines with bromine very slowly, and after twenty-four hours yields a *bromo*-compound, $(C_{12}H_{12}O_2Br)_x$, the amount of bromine uniting with the ester being only half that which would have been combined had the allyl groups remained intact.

Both polymerides are hydrolysed by alcoholic potassium hydroxide to the corresponding *acids*, which form white, amorphous powders, sintering at 180—190° (decomp. 210—220°), and closely resemble one another

The above esters differ from that obtained by the polymerisation of allyl cinnamate by exposure to light, in solubility, and in being hydrolysed by alkalis.

Allyl cinnamate combines almost instantly with bromine (1 mol.) in chloroform solution, yielding *αβ-dibromopropyl cinnamate* as a viscid oil. Combination with a second molecule takes place more slowly, resulting in the formation of *αβ-dibromopropyl αβ-dibromopropionate*, which crystallises in white needles, m. p. 69—71°.

On exposure to light for nine months, allyl cinnamate yields a *polymeride*, which is precipitated by methyl alcohol in white flocks, m. p. above 300°, and is not hydrolysed by alcoholic potassium hydroxide.

The *polymerides* of benzyl cinnamate (decomp. 270°) and octyl cinnamate have been prepared in a similar manner.   F. B.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. VIII. Derivatives of Orsellinic and α-Resorcylic [3 : 5-Dihydroxybenzoic] Acids. EMIL FISCHER and HERMANN O. L. FISCHER (*Ber.*, 1913, 46, 1138—1148).—The difficulties attendant on the conversion of dimethylcarbonato-orsellinic acid (3 : 5-dimethylcarbonato-*o*-toluic acid) into its chloride have been overcome (compare A., 1912, i, 860). By coupling the latter with orsellinic acid, the authors have been able to prepare dimethylcarbonato - orsellinoylorsellinic acid (annexed formula), which, when hydrolysed, gives a diorsellinic acid identical with the natural lecanoric acid. A series of compounds has also been prepared from α-resorcylic acid.

Dimethylcarbonato-orsellinyl chloride, $C_6H_2Me(O \cdot CO_2Me)_2 \cdot COCl$,
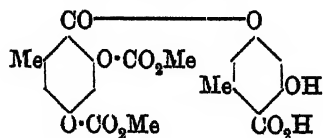
m. p. 53—54°, is obtained by the action of phosphorus pentachloride on dimethylcarbonato-orsellinic acid suspended in chloroform. In suitable circumstances it reacts readily with ethyl alcohol, the corresponding *ethyl* ester being probably formed. In alkaline acetone solution it condenses with *p*-hydroxybenzoic acid, forming 4-dimethylcarbonato-orsellinoyloxybenzoic acid,

$$C_6H_2Me(O \cdot CO_2Me)_2 \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H,$$
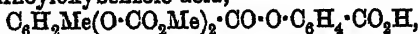
m. p. 203—205° (corr. decomp.), after previous softening at about 190°, which in aqueous alcoholic solution does not give a characteristic coloration with ferric chloride. The alkaline salts are sparingly soluble in water. When heated with ammonia, the didepside, *4-orsellinoyloxybenzoic acid,* is obtained. Difficulty was experienced in obtaining the latter in the crystalline form until a nucleus of the crystalline acid was isolated by decomposition of the *pyridine* salt. The air-dried acid contains $1H_2O$. It has m. p. about 209° (corr. decomp.) after previous softening at about 180°, the value found depending greatly on the mode of heating.

Dimethylcarbonato-orsellinoylorsellinic acid, needles, m. p. 185—187° (corr. decomp.), is obtained by the gradual addition of a solution of dimethylcarbonato-orsellinoyl chloride in acetone to a well-cooled solution of orsellinic acid in acetone and *N*-sodium hydroxide. In aqueous alcoholic solution it gives an intense reddish-violet coloration with ferric chloride. By repeated treatment with methyl chloroformate and alkali in aqueous acetone solution, it yields a crystalline *product,* which gives no coloration with ferric chloride. This can be separated by means of potassium carbonate into a soluble portion, probably *trimethylcarbonatolecanoric acid,* and an insoluble portion which is being investigated. Aqueous sodium hydroxide slowly converts dimethylcarbonato-orsellinoylorsellinic acid into lecanoric acid, colourless needles, having no definite m. p. When quickly heated it softens at about 170°, and is completely melted at 175° with brisk evolution of gas. The air-dried acid contains $1H_2O$. Identity of this product with natural lecanoric acid was established by comparison of m. p., colorations with ferric chloride and bleaching powder, solubility, and crystal form of the two substances, and, further, by the transformation of each into the *trimethyl ether* of *methyl lecanorate,* $C_{30}H_{22}O_7$. The product from the synthetic acid had m. p. 147—148° (corr.), whilst that from the natural acid had m. p. 146—147° (corr.) after softening at 140°. A mixture of the two had m. p. 145—146·5°.

3 : 5-*Dimethylcarbonatobenzoic acid,* prepared by the action of methyl chlorocarbonate on a solution of 3 : 5-dihydroxybenzoic acid in *N*-sodium hydroxide, has m. p. 161—164° (corr.) after slight previous softening. Phosphorus pentachloride converts it into the corresponding *chloride,* colourless needles, m. p. 109—110° (corr.), which, when coupled with *p*-hydroxybenzoic acid in the usual manner, yields 4-(3 : 5-dimethylcarbonatobenzoyl)oxybenzoic acid, $C_6H_3(O \cdot CO_2Me)_2 \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H$, needles, m. p. 161—163° (corr.).

When treated with aluminium chloride and benzene during an hour at 70—75°, and then during forty-five minutes at 75—80°, 3 : 5-dimethylcarbonatobenzoyl chloride yields 3 : 5-*dihydroxybenzophenone,* which separates from water with $1H_2O$. The dry substance has m. p.

160—162° (corr.). If the temperature in the above process is maintained at 40—45° during five hours, no hydrogen chloride is evolved, and a pale yellow *oil* is subsequently obtained, which crystallises when brought into contact with light petroleum. The product, which has not yet been obtained in the pure state, contains the methylcarbonato-groups, and is transformed by alkali into 3 : 5-dihydroxybenzophenone. H. W.

Tannin and the Synthesis of Similar Substances. III. Compounds of High Molecular Weight. EMIL FISCHER and KARL FREUDENBERG (*Ber.*, 1913, **46**, 1116—1138).—The authors have continued their previous work (A., 1912, i, 471, 887), and describe a convenient method of preparing *m*-digallic acid in larger quantities. The properties of this acid resemble those of the digallic acid previously described as the para-compound (A., 1908, i, 893) so closely that the two substances are in all probability identical. It differs considerably, however, from the *m*-digallic acid described by Nierenstein (A., 1910, i, 265).

A series of compounds of high molecular weight has been obtained by the use of tribenzoylgallic acid ; for example, hexa-(tribenzoylgalloyl)-mannitol. In the analysis of this and similar compounds, a difficulty is experienced in that the differences in the percentages of carbon and hydrogen are not sufficiently great to allow conclusions to be drawn with regard to the number of acyl groups present. This has been overcome by the introduction of halogen atoms into the molecule, and a series of substances has been prepared from 2 : 4 : 6-tribromophenol-*d*-glucoside and *p*-iodophenylmaltosazone, of which the most interesting is *hepta-(tribenzoylgalloyl)-p-iodophenylmaltosazone,*

$$C_{220}H_{142}O_{58}N_4I_2,$$
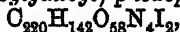
mol.-wt. 4021. The molecular weight of this and similar substances has been determined in bromoform solution, the observed values being found to agree with those theoretically required without greater divergence than is frequently encountered with much more simply constituted, crystalline substances.

Carbonylogallic acid (4 : 5 - *carbonato* - 3 - *hydroxybenzoic acid*), $OC{<}^O_O{>}C_6H_2(OH)\cdot CO_2H$, is obtained by the addition of a solution of carbonyl chloride in toluene to a well-cooled mixture of gallic acid, acetone, and 2*N*-sodium hydroxide (3 mols.), and subsequent acidification of the product with hydrochloric acid. A full description of the apparatus employed is given. The acid has m. p. about 255° (corr. decomp.). It is sparingly soluble in cold water, and decomposed by hot water with regeneration of gallic acid. Hot methyl alcohol converts it into 3-methylcarbonatogallic acid. In alcoholic solution it gives a faint coloration with ferric chloride, which increases in intensity on keeping. It is transformed by diazomethane into *methyl 4 : 5-carbonato-3-methoxybenzoate,* $OC{<}^O_O{>}C_6H_2(OMe)\cdot CO_2Me$, long needles, m. p. 134° (corr.), which, when boiled with water, probably yields methyl 4 : 5-dihydroxy-3-methoxybenzoate. The latter is converted by the successive action of sodium hydroxide and hydro-

chloric acid into 4 : 5-dihydroxy-3-methoxybenzoic acid, which is apparently identical with the acid obtained by Vogl (A., 1899, i, 698). The latter gives m. p. 199—200° (uncorr.), whereas the authors find about 220° (corr. decomp.), but point out that the observed m. p. depends greatly on the mode of heating.

m-Digallic acid is prepared by the alternate addition of N-potassium hydroxide and of a solution of trimethylcarbonatogalloyl chloride in acetone to a cooled solution of carbonylogallic acid in acetone and N-potassium hydroxide. The product is treated with N-sodium hydroxide and subsequently with hydrochloric acid, when m-digallic acid, needles, m. p. about 280° (corr. decomp.) after softening at 260° (corr.), is obtained, the yield being 45% of the theoretical. The acid dissolves in water at 25° in the proportion 1 : 860, and gives a deep bluish-black coloration with ferric chloride. With aqueous potassium cyanide solution, it yields, after ten seconds, a pink coloration which disappears after a time, but returns on shaking the solution. When boiled during six hours with 1% hydrogen peroxide solution, it yields a dark brown coloration, but no precipitate. With 10% aqueous hydrogen peroxide under similar conditions, a clear solution is formed. In these particulars, the acid differs markedly from Nierenstein's m-digallic acid (*loc. cit.*). With diazomethane, it yields methyl 5(3′ : 4′ : 5′)-trimethoxybenzoyloxy-3 : 4-dimethoxybenzoate, which is identical with the product obtained previously (A., 1912, i, 888). Acetic anhydride converts it into *penta-acetyl-m-digallic* acid, needles, m. p. 193—194° (corr.), after softening at about 184° (Nierenstein's m-digallic acid gave a penta-acetyl derivative, m. p. 211—214°). An attempt to prepare the corresponding pentabenzoyl derivative was unsuccessful.

3 : 4 : 5-*Trimethoxybenzoic anhydride*, microscopic needles, m. p. 160—161° (corr.), is obtained by the action of 3 : 4 : 5-trimethoxybenzoyl chloride on 3 : 4 : 5-trimethoxybenzoic acid in chloroform solution in the presence of quinoline. Similarly, the mixed *anhydride* of 3 : 4 : 5-trimethoxybenzoic acid and pentamethyl-m-digallic acid, needles, m. p. 165—166° (corr.), is obtained from 3 : 4 : 5-trimethoxybenzoyl chloride and pentamethyl-m-digallic acid, and is identical with a product previously obtained during the synthesis of pentamethyl-m-digallic acid (A., 1912, i, 888).

Pentamethyl-p-digallic acid is obtained in 75% yield from 3 : 4 : 5-trimethoxybenzoyl chloride and syringic acid according to the method employed in preparing the m-isomeride. It forms leaflets, m. p. 221—222° (corr.). The methyl ester, prepared by the action of diazomethane on the acid, has m. p. 172—173° (corr.), whereas Mauthner (A., 1911, i, 725) found m. p. 169—170°.

Tribenzoylgallyl chloride, $C_6H_2(OBz)_3 \cdot COCl$, needles, m. p. 124—126° (corr.), is obtained by the action of phosphorus pentachloride on tribenzoylgallic acid in the presence of chloroform at the ordinary temperature. The corresponding ethyl *ester* has m. p. 126—128° (corr.), whilst the *anhydride*, $C_{56}H_{34}O_{15}$, needles, has m. p. 195—196°, and is more stable towards alcohol than simple substances of this class.

Tetra-(tribenzoylgalloyl)-tribromophenol-d-glucoside,
$$(C_{28}H_{17}O_7)_4 C_6H_7O_6 \cdot C_6H_2Br_3,$$

is prepared by the addition of tribromophenol-d-glucoside to a solution of tribenzoylgalloyl chloride and quinolin in chloroform. It is a white, amorphous powder, which softens at about 130°, and melts to a clear syrup at about 155°. In tetrachloroethane solution, it has $[\alpha]_D^{20} - 31\cdot01°$. *Hexa-(tribenzoylgalloyl)-mannitol*, obtained in a similar manner, has $[\alpha]_D^{20} + 19\cdot63°$ in tetrachloroethane solution. It soften at about 125°, and is completely molten at about 150°.

Tetrabenzoylphenylglucosazone, $C_6H_6O_4Bz_4(N_2HPh)_2$, softens at about 100°, is completely molten at about 130°, and begins to decompose at about 140°. When dissolved in acetylene tetrachloride, it has $[\alpha]^{20} - 12\cdot16°$ for the Auer light.

p-*Iodophenylmaltosazone*, $C_{12}H_{20}O_9(N_2H\cdot C_6H_4I)_2$, prepared by the action of p-iodophenylhydrazine on maltosone in aqueous-alcoholic solution, crystallises in yellow needles, m. p. 208° (corr.), after slight previous softening, the m. p., however, varying according to the mode of heating. The solution in pyridine exhibits mutarotation, constant values being probably obtained after three days. For one specimen, $[\alpha]_D^{20}$ was found to be $+83\cdot44°$ after eight minutes, $+66\cdot51°$ after thirty-two hours, $+66\cdot11°$ after forty-eight hours. When treated with tribenzoylgalloyl chloride at the ordinary temperature in the presence of quinoline and chloroform, p-iodophenylmaltosazone yields *hepta-(tribenzoylgalloyl)-p-iodophenylmaltosazone*,

$$(C_{28}H_{17}O_7)_7C_{12}H_{13}O_9(N_2H\cdot C_6H_4I)_2,$$
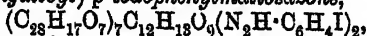
amorphous, pale yellow powder, which softens at about 145°, and is melted to a red liquid at 160°. In tetrachloroethane solution it has $[\alpha]^{20} - 8\cdot75°$.

The molecular weight of the above substances of high molecular weight was determined cryoscopically in bromoform solution, care being taken to obtain them free from any trace of adhering solvent. From experiments on the molecular weight of naphthalene dissolved in bromoform, the value 143 was adopted as constant for the solvent. The following mean results were obtained, the theoretical values being enclosed in brackets : tribenzoylgallic anhydride, 954 (946) ; tetra-(tribenzoylgalloyl)-tribromophenol-d-glucoside, 2036 (2349) ; hexa-(tri-benzoylgalloyl)-mannitol, 2781 (2967) ; hepta-(tribenzoylgalloyl)-p-iodophenylmaltosazone, 3503 (4021). H. W.

Salicylaldehydephenylhydrazone. GEORG LOCKEMANN and FRANZ LUCIUS (*Ber.*, 1913, 46, 1012—1021. Compare this vol., i, 296).—Salicylaldehyde phenylhydrazone (compare Biltz, A., 1894, 584) can appear in isomeric forms, which, however, do not differ in melting point, but in crystalline form, colour, and solubility. Their formation depends on the conditions of crystallisation and the illumination. The isomerism is therefore physical and not chemical, as supposed by Biltz.

The α-hydrazone is formed in rectangular prisms on slow crystallisation from dilute alcohol or benzene ; these are pale or dark green when light is excluded, greyish or brownish-yellow in its presence. The green form occurs in presence of acetic acid ; with ammonia the yellow modification is formed.

The β-hydrazone is deposited on quick crystallisation in colourless

needles, which become greenish-yellow on exposure to light. The γ-modification separates from light petroleum in bunches of green needles, which become yellow or orange on exposure. In all three modifications the coloration brought about by light slowly reverses in the dark. All three soften between 135° and 140°, m. p. 142—143°.

When benzoylated in pyridine solution, according to the proportion of benzoyl chloride, the *O*-monobenzoyl or the *O,N*-dibenzoyl derivatives are obtained. When sodium hydroxide is present, the dibenzoyl derivative is the main product, more or less hydrazone remaining unattacked.

On reduction of the dibenzoyl derivative with zinc dust and acetic acid, benzanilide and *o*-hydroxybenzylbenzamide,

$$OH \cdot C_6 H_4 \cdot CH_2 \cdot NH \cdot CO \cdot C_6 H_5,$$
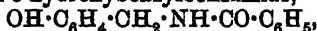
are formed.

o-Benzoylhydroxybenzylbenzamide, prepared by benzoylating by the Schotten-Baumann process, forms colourless needles, m. p. 141—142°.

When hydrolysed either with cold alcoholic potassium hydroxide or warm alcoholic ammonia, *N*-benzoyl *o*-hydroxybenzaldehydephenyl-hydrazone is obtained; it gives a dark bluish-green ferric chloride coloration. E. F. A.

Condensation Product of Piperonaldehyde with Ethyl Urethane. I. G. BIANCHI (*Gazzetta*, 1913, 43, i, 237—243).— When these substances are heated for half an hour on the water-bath with a little hydrochloric acid, *piperonylidenebisurethane*, $C_{15}H_{18}O_6N_2$, m. p. 177—178°, is obtained; it crystallises in colourless needles. R. V. S.

Preparation of Cyclic Ketones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 256622).—When adipic acid, its homologues, or substitution products are heated they furnish satisfactory yields of the corresponding cyclic ketones; this reaction is conveniently carried out under reduced pressure, in the presence of an inert gas, and of a catalytic reagent, such as oxides, carbonates or other salts of the alkali metals, alkaline earths, or magnesium; of salts of the heavy metals, such as iron, nickel, cobalt, manganese, or uranium; or of phosphoric, boric, or other acids.

*cyclo*Pentanone, b. p. 49—50°/31 mm., is obtained in quantitative yield from adipic acid at 290—295° in the presence of barium hydroxide; with uranium nitrate the yield is 85%, and with ferrous sulphate 90%.

2-Methyl*cyclo*pentanone, b. p. 38°/11 mm. and 57—59°/29 mm., is similarly obtained at 300—305° from β-methyladipic acid, whilst suberic acid furnishes *suberone* (b. p. 179°) at 320—325° in the presence of iron. F. M. G. M.

Terpenes and Ethereal Oils. CXV. OTTO WALLACH (*Annalen*, 1913, 397, 181—219).—A systematic examination has hitherto not been made of the problem how the position of the oxygen atom in a cyclic ketone influences the b. p. Recent examples in the literature

lead the author to the generalisation that in saturated, isomeric, cyclic ketones containing the same substituents the b. p. is lowest when the heaviest substituent is nearest to the oxygen atom and highest when this substituent is situated as far as possible from the oxygen atom. Since dihydro*iso*camphor has b. p. 211° and carvomenthone has b. p. 220—221°, the generalisation furnishes corroborative evidence that dihydro*iso*camphor is not 1-methyl-5-*iso*propyl*cyclo*-hexan-2-one (compare A., 1912, i, 878).

Much more complicated and difficult is the problem of the relations between the constitutions and the b. p.'s of unsaturated cyclic ketones, since in such substances the position of the ethylenic linking must also be taken into account. By reference to the b. p.'s and the constitutions of many unsaturated cyclic ketones, the author shows that (i) ketones in which the ethylenic group and the carbonyl group form a conjugated system have a higher b. p. than isomeric ketones in which such a system does not obtain, and, moreover, that the b. p. is higher when the ethylenic linking in the conjugated system is part of the carbo-cyclic nucleus than when it is attached semicyclically or is present in a side-chain; for example, Δ^1-menthen-3-one, b. p. 235°, pulegone, b. p. 221—222°, and also carvenone, b. p. 232—233°, and dihydro-carvone, b. p. 221—223°; (ii) the replacement of the hydrogen atom in the system $\cdot C{:}CH{\cdot}CO\cdot$ by an alkyl group R is accompanied by a fall in the b. p. which is the more pronounced the greater is the molecular weight of R; for example, 1-methyl-5-*iso*propyl-Δ^1-*cyclo*hexen-3-one, b. p. 244°, Δ^1-menthen-3-one, b. p. 235°, carvotanacetone, b. p. 228—229°, 1-methyl-2-*iso*propyl-Δ^1-*cyclo*hexen-3-one, b. p. 216—217°, and Δ^4-menthen-3-one, b. p. 211°, and (iii) the fall in the b. p. by the conversion of unsaturated ketones of the type ⬡—COMe into saturated ketones of the type $C_6H_{11}\cdot COMe$ is about 19°, and is therefore distinctly greater than the fall, about 3—4°, in the b. p. caused by the conversion of ⬡—$CH_2{\cdot}COMe$ into $C_6H_{11}{\cdot}CH_2{\cdot}COMe$.

1:4-Dimethyl-Δ^6-cyclohexen-2-oneoxime, $NOH{:}C{<}^{CMe{=\!=}CH}_{CH_2\cdot CHMe}{>}CH_2$, m. p. 92—93°, and another *substance*, m. p. 169°, which is apparently an isomeride, are obtained by warming the nitrosochloride of 1:4-dimethyl-Δ^1-*cyclo*hexene with sodium acetate in glacial acetic acid. By hydrolysis, the former yields *1:4-dimethyl-Δ^6-cyclohexen-2-one* b. p. 189—190°, D^{22} 0·938, n_D^{22} 1·4753 (*semicarbazone*, m. p. 165°), which is oxidised to *p*-xylenol by ferric chloride and glacial acetic acid.

By reduction of Paal's method, 1:4-dimethyl-Δ^6-*cyclo*hexen-2-one yields 1:4-dimethyl*cyclo*hexan-2-one, b. p. 178°, D^{20} 0·9025, n_D^{20} 1·4446 (oxime, m. p. 108—109°, semicarbazone, m. p. 175—176°), which is also obtained by warming 1:4-dimethyl*cyclo*hexan-1:2-diol with dilute sulphuric acid. The saturated ketone and its oxime and semicarbazone have been described, frequently but erroneously, in the literature. By oxidation with chromic and dilute sulphuric acids, it is converted into δ-acetyl-β-methylvaleric acid (semicarbazone, m. p. 146—147°), which in turn is oxidised to β-methyladipic acid by sodium hypobromite.

By reactions similar to the preceding, tetrahydro-*m*-xylene nitroso-chloride is converted successively into 1 : 3-*dimethyl-Δ²-cyclohexen-4-oneoxime*, 1 : 3-*dimethyl-Δ²*-cyclohexen-4-one (*semicarbazone*, m. p. 194—195°), and 1 : 3-dimethyl*cyclo*hexan-4-one (this vol., i, 278).

1- imethyl*cyclo*hexan-5-one, b. p. 181·5—182°, D¹⁹ 0·895, n_D 1·4425 (semicarbazone, m. p. 201°), and 1 : 3-dimethyl*cyclo*hexan-2-one, b. p. 174·5°, D²⁰ 0·9140, n_D 1·4476 (oxime, m. p. 114—115°, semi-carbazone, m. p. 176—177°), have been prepared and their physical constants and those of the oximes and semicarbazones compared with the values recorded by other investigators.

[With LOUIS AUGSPURGER.]—By reactions similar to the preceding, 1-methyl-4-ethyl-Δ³-*cyclo*hexene nitrosochloride has been converted successively into 1-*methyl-4-ethyl-Δ³*-cyclohexen-5-oneoxime, m. p. 59—60°, 1-*methyl-4-ethyl-Δ³*-cyclohexen-5-one, b. p. 203—204°, D¹⁹ 0·9310, n_D 1·4759 (*semicarbazone*, m. p. 152—153°), and 1-methyl 4-ethyl*cyclo*hexan-5-one, b. p. 197°, D²⁰ 0·9000, n_D 1·4485 (semicarbazone, m. p. 178—181°, oxime, m. p. 80°). By oxidation with chromic acid the last substance yields a ketonic *acid*, $CO_2H·CH_2·CHMe·CH_2·CH_2·COEt$ (*semicarbazone*, m. p 145°.

1-iso*Propyl*cyclo*hexan-4-one*, b. p. 214—214·5°, D¹⁹ 0·9175, n_D^{19} 1·4561, (*dibenzylidene* compound, m. p. 105°), is obtained by the reduction of 1-*isopropyl-Δ¹-cyclo*hexen-4-one (A., 1908, i, 424) by Paal's method. 1-Methyl-3-*isopropyl-Δ⁶-cyclo*hexen-5-one, b. p. 244° (decomp.), D²¹ 0·9340, n_D^{21} 1·4865 (semicarbazone, m. p. 167°), is reduced by Paal's method to 1-methyl-3-*iso*propyl*cyclo*hexan-5-one, b. p. 221—223°, D²⁰ 0·8965, n_D 1·4541.

[With RUD. MÜLLER and FR. HENJES.]—The low b. p., 212°, of Δ⁴-menthen-3-one, in comparison with those of the isomerides, Δ¹-menthen-3-one, 235—237°, carvenone, 232—233°, and carvotan-acetone, 228—229°, led the authors to the opinion that an error must have been made either in the b. p. or in the constitution (compare Auwers, A., 1909, i, 592). It is now shown that no error had been committed. *i*-Δ⁴-Menthen-3-one, prepared from *i*-menthene, has b. p. 212—213°, D²⁰ 0·9165, n_D 1·4726, whilst *l*-Δ⁴-menthen-3-one, prepared from menthol, is a yellow liquid having b. p. 211—212°, D¹⁸ 0·919, n_D 1·4729, and [α]_D − 67·46° in methyl alcohol. The active substance forms a *semicarbazone*, m. p. 170—171°, and a *dibenzylidene* derivative, yellow needles, m. p. 140—141°, [α]_D − 58·41° in chloroform. The constitution of the active menthenone is proved by its reduction to *l*-menthone by Paal's method, and ultimately to *l*-menthol by sodium and alcohol. The constitution of the *i*-menthenone has been proved by the synthesis of the ketone from 1-methyl*cyclo*hexan-4-one and magnesium *iso*propyl iodide, the resulting alcohol being dehydrated by dilute sulphuric acid, and the 1-methyl-4-*iso*propyl-Δ³-*cyclo*hexene being converted through the nitrosochloride into the menthenoneoxime. The low b. p. of Δ⁴-menthen-3-one, therefore, must be due to the position of the *iso*propyl group between the carbonyl group and the ethylenic group (compare above).

[With FR. HENJES.]—Since little is accurately known of the deriv-atives of *i*-menthone, a large quantity of this ketone has been prepared by reducing Δ¹-menthen-3-one by Paal's method. It has b. p. 210°,

D^{20} 0·8975, n_D 1·4521, and forms a semicarbazone, m. p. 212°, oxime, m. p. 79—80° (benzoyl derivative, m. p. 69—70°), *isooxime*, m. p. 87—88°, hydrochlorobenzylidene derivative, m. p. 119—120°, and yields a mixture of menthols by reduction. The reduction of *i*-menthoneoxime yields *i*-menthylamine, b. p. 208°, which forms a hydrochloride, m. p. above 250°, carbamide, m. p. 151—152°, phenylmenthylcarbamide, m. p. 135—136°, phenylthiocarbamide, m. p. 136—137°, and benzylidene compound, m. p. 141—142°. C. S.

Pinacolin Transformation. II. Asymmetric Cyclic and Acyclic Pinacones and Their Transformation Products. HANS MEERWEIN (*Annalen*, 1913, **396**, 200—263. Compare A., 1910, i, 856).—A thorough examination of the reaction whereby 1-*iso*propyl*cyclo*pentane-1-α-diol is converted into 1 : 1-dimethyl*cyclo*hexan-2-one and of analogous reactions has led to the following important generalisations in connexion with the pinacolin transformation : (i) the pinacolin transformation is a true, intramolecular, atomic rearrangement ; intermediate products cannot be isolated ; (2) the course of the transformation is conditioned by different factors depending on the structure of the pinacone. In symmetric pinacones of the type $CRR'(OH) \cdot CRR' \cdot OH$, the transformation depends only on the relative ease of mobility of the groups R and R′, whilst in asymmetric pinacones, $CR_2(OH) \cdot CR'_2 \cdot OH$, the stability of the hydroxyl groups is the determining factor ; (3) by a study of the pinacolin transformation, it is possible, not only experimentally to ascertain the different stabilities (that is, the strength of their attachment to the carbon atoms) of the hydroxyl groups in asymmetric pinacones, but also, since such stability is determined mainly by the stabilities of the radicles attached to the same carbon atom, the relative strengths of the attachment of these radicles.

[With HANS PROBST.]—The interaction of methyl *cyclo*pentan-1-ol-1-carboxylate and an excess (4—5 mols.) of magnesium ethyl bromide or magnesium phenyl bromide leads by the usual method to the formation of 1-*hydroxy*-1-α-*ethylpropylcyclo*pentan-1-*ol*,

$$\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} \!\!>\!\! C(OH) \cdot CEt_2 \cdot OH,$$
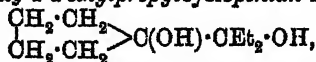
m. p. 39·5°, b. p. 136°/25 mm., and 1-α-*hydroxybenzhydrylcyclo*-pentan-1-*ol*, $\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} \!\!>\!\! C(OH) \cdot CPh_2 \cdot OH$, m. p. 125°, colourless prisms, respectively. The former is converted by concentrated sulphuric acid at −10° into a mixture of 1 : 1-*diethylcyclo*hexan-2-*one*,

$$CH_2 \!<\!\! \begin{matrix} CH_2 - CO \\ CH_2 - CH_2 \end{matrix} \!\!>\!\! CEt_2,$$
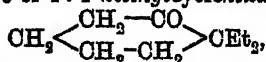
b. p. 93·5°/15 mm., D^{20} 0·9236, n_D^{20} 1·4621 (the constitution of which is proved by its oxidation to αα-*diethyladipic acid*,

$$CO_2H \cdot CEt_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H,$$
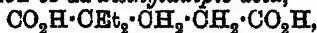
m. p. 90—92°, by nearly boiling 30% nitric acid), and 1-*propionyl*-1-*ethylcyclo*pentane, $\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} \!\!>\!\! CEt \cdot COEt$, b. p. 86°/16 mm., D^{20} 0·9104, n_D^{20} 1·4525, which is oxidised to 1-*ethylcyclo*pentane-1-*carboxylic acid*,

m. p. − 8°, b. p. 132°/18 mm., by nearly boiling 40% nitric acid. The separation of the mixture is readily effected by means of the semicarbazones, the *semicarbazone*, m. p. 202—203°, rhombic leaflets, of the *cyclo*hexane derivative being sparingly soluble in alcohol or other solvents, whilst the *semicarbazone*, m. p. 148·5°, slender needles, of the *cyclo*pentane derivative is easily soluble.

The pinacolin transformation of 1-α-hydroxybenzhydryl*cyclo*pentan-1-ol by cold concentrated sulphuric acid yields only 1 : 1-*diphenylcyclohexan-2-one*, m. p. 99°, stout needles (*semicarbazone*, m. p. 240°), by the oxidation of which by chromic and acetic acids benzophenone is produced.

[With F. KREMERS.]—The product of the pinacolin transformation of 1-*iso*propyl*cyclo*hexane-1-α-diol contains about 33% of 1:1-*dimethylcycloheptan-2-one* (*semicarbazone*, m. p. 169°) in addition to the 1-acetyl-1-methyl*cyclo*hexane described by Tarbouriech.

1-α *Hydroxybenzhydrylcyclohexan-1-ol,*

$$CH_2 \underset{CH_2 \cdot CH_2}{\overset{CH_2 \cdot CH_2}{\diagup \diagdown}} C(OH) \cdot CPh_2 \cdot OH,$$
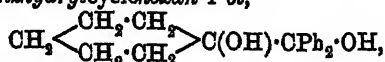
m. p. 130°, stout prisms, prepared from methyl*cyclo*hexan-1-ol-1-carboxylate and magnesium phenyl bromide, is transformed by concentrated sulphuric acid at 0° into the *ethylene oxide,*

$$CH_2 \underset{CH_2 \cdot CH_2}{\overset{CH_2 \cdot CH_2}{\diagup \diagdown}} C \underset{CPh_2}{\overset{O}{\diagup \diagdown}},$$
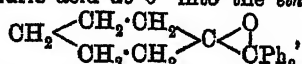
m. p. 92—94°, rhombic prisms, which does not react with semicarbazide and is oxidised to benzophenone, glutaric and adipic acids by chromic and acetic acids.

[With F. KREMERS and R. SPLITTEGARB.]—Ethyl 9-hydroxyfluorene-9-carboxylate reacts in the usual manner with an excess, 7—8 mols., of magnesium methyl iodide, magnesium ethyl bromide, or magnesium phenyl bromide to form, ultimately, 9-*β-hydroxyisopropylfluorenol,*

$$\underset{C_6H_4}{\overset{C_6H_4}{\diagdown \diagup}} C(OH) \cdot CMe_2 \cdot OH,$$ m. p. 101°, large, colourless needles,

9-*hydroxydiethylmethylfluorenol,* $\underset{C_6H_4}{\overset{C_6H_4}{\diagdown \diagup}} C(OH) \cdot CEt_2 \cdot OH,$ m. p. 106°,

colourless needles, and 9-α-*hydroxybenzhydrylfluorenol,*

$$\underset{C_6H_4}{\overset{C_6H_4}{\diagdown \diagup}} C(OH) \cdot CPh_2 \cdot OH,$$
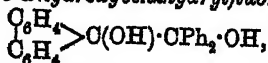
m. p. 160—162°, slender needles, respectively. By cold concentrated sulphuric acid the first is transformed into 9-*acetyl-9-methylfluorene,* $\underset{C_6H_4}{\overset{C_6H_4}{\diagdown \diagup}} CMe \cdot COMe,$ m. p. 89°, b. p. 181°/18 mm. (*semicarbazone,* m. p. 254—256°), the second into 9-*propionyl-9-ethylfluorene,* m. p. 58° (*semicarbazone,* m. p. 236°), and the last, which is readily decomposed into benzophenone and fluorenol by 10% alcoholic potassium hydroxide, into 9 : 9-*diphenylphenanthrone,* $\underset{C_6H_4 \cdot CO}{\overset{C_6H_4 \cdot CPh_2}{| \quad |}}$, m. p. 197°, rhombic prisms.

The constitution of 9-acetyl-9-methylfluorene is proved by its decomposition into 9-methylfluorene and acetic acid by alcoholic potassium hydroxide, and by its oxidation to 9-*methylfluorene-9-carboxylic acid,*

m. p. 166°, glistening leaflets, by 10% sodium hypobromite. 9 : 9-Di-phenylphenanthrone is identical with the substance described as *s*-diphenyldiphenylene-ethylene oxide by Werner and Grob, but that it has the constitution denoted by its name is proved by the fact that it yields the acid, $CHPh_2 \cdot C_6H_4 \cdot C_6H_4 \cdot CO_2H$, by heating with alcoholic potassium hydroxide. Similarly, the pinacolins obtained by Zincke and Tropp from a series of pinacones prepared from phenanthra-quinone and magnesium alkyl haloids, and regarded by them as α-pinacolins (*s*-dialkyldiphenylene-ethylene oxides), are probably 9 : 9-di-alkylphenanthrones, since the methyl compound (9 : 9-dimethyl-phenanthrone), for example, is converted into 2-iso*propyldiphenyl-2'-carboxylic acid*, $CHMe_2 \cdot C_6H_4 \cdot C_6H_4 \cdot CO_2H$, m. p. 104—106°, by potassium hydroxide at 220—240°.

[With R. SPLITTEGARB.]—Acyclic, asymmetric pinacones have been prepared as similar as possible in structure to the preceding cyclic pinacones. Methyl α-hydroxy*iso*butyrate reacts with magnesium ethyl or phenyl bromide to form, ultimately, β-*methyl-γ-ethylamylene βγ-glycol*, $OH \cdot CMe_2 \cdot CEt_2 \cdot OH$, b. p. 99—101°/19 mm., and αα-*di-phenyl-β-methylpropylene glycol*, $OH \cdot CPh_2 \cdot CMe_2 \cdot OH$, m. p. 91°, respectively. βγ-*Dimethylamylene βγ-glycol*, $OH \cdot CMe_2 \cdot CMeEt \cdot OH$, b. p. 94—95°/21 mm., is prepared from *methyl methylethylglycollate*, b. p. 151·6—152° (the *ethyl* ester has b. p. 162°, and the *acid* itself has b. p. 133—134°/16 mm.), and magnesium methyl iodide.

β-Methyl-γ-ethylamylene βγ-glycol is transformed by concentrated sulphuric acid into *ethyl* tert.-*amyl ketone*, $CMe_2Et \cdot COEt$, b. p. 150·5—152°, D^{20} 0·8298 (*semicarbazone*, m. p. 98°), the constitution of which is proved by its oxidation to αα-dimethylbutyric acid by aqueous sodium hypobromite. By the pinacolin transformation, βγ-dimethylamylene βγ-glycol yields *methyl* tert.-*amyl ketone*,

$$CMe_2Et \cdot COMe,$$
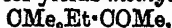
b. p. 130 6°, D^{20} 0·8243 (*semicarbazone*, m. p. 136—138°), which also yields αα-dimethylbutyric acid by oxidation. αα-Diphenyl-β-methyl-propylene-αβ-glycol is transformed by cold concentrated sulphuric acid into methyl αα-diphenylethyl ketone, m. p. 41°, which is oxidised to αα-diphenylpropionic acid by sodium hypobromite.

[With F. KREMERS.]—*Bromodiphenylacetic acid*, $CPh_2Br \cdot CO_2H$, m. p. 133—134°, prepared from benzilic acid and hydrogen bromide in glacial acetic acid at 0°, is readily converted by methyl alcohol and sulphuric acid into methyl methoxydiphenylacetate, b. p. 191°/16 mm., m. p. 29°, which reacts with magnesium methyl iodide to form, ultimately, γ-*methoxy-γγ-diphenyl-β-methylpropane-β-ol*,

$$OMe \cdot CPh_2 \cdot CMe_2 \cdot OH,$$
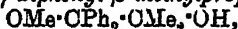
m. p. 45—47°, b. p. 181—182°/16 mm.; the latter is converted by cold concentrated sulphuric acid into methyl αα-diphenylethyl ketone, not into ω-phenyl-ωω-dimethylacetophenone.

[By the AUTHOR.]—The various explanations of the pinacolin trans-formation are stated and criticised. The most widely accepted theory assumes the intermediate formation of ethylene oxides, but is not in agreement with observations of the author, Tiffeneau, Montagne, and others. The formation of tangible, intermediate products has not been observed, the transformation occurring by loss of water and the

migration of one group. The water must be eliminated before the migration occurs, because s- and as-diphenylmethylpropylene glycol yield the same pinacolin, $CPh_2Me\cdot COMe$, and s- and as-dimethyldiethylethylene glycol also produce the same pinacolin, $CMe_2Et\cdot COEt$. If these changes are explained by an interchange in position of a hydroxyl and an alkyl or aryl group and subsequent elimination of water, the author claims that sometimes one group, sometimes another, changes position with the hydroxyl group without any regularity or obvious reason.

The first step in the transformation, therefore, is

$$OH\cdot CR_2\cdot CR_2\cdot OH \longrightarrow \cdot CR_2\cdot CR_2\cdot O\cdot.$$
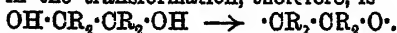
The complex then changes to a stable state, either $O{<}{\small\begin{matrix}CR_2\\[-2pt] |\\[-2pt] CR_2\end{matrix}}$, which

is quite exceptional, or $CR_3\cdot COR$. Symmetric pinacones,

$$OH\cdot CRR'\cdot CRR'\cdot OH,$$
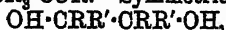
contain hydroxyl groups of like function, and therefore yield, by loss of water, the complex $\cdot CRR'\cdot CRR'\cdot O\cdot$. The final state of this complex depends on the relative mobilities of R and R'; in general, the methyl group migrates more readily than its homologues, aliphatic groups less readily than aromatic, and substituted aromatic groups more readily than the phenyl radicle. In asymmetric pinacones, $OH\cdot CR_2\cdot CR'_2\cdot OH$, the hydroxyl groups are not of similar function, and, therefore, the first step of the pinacolin transformation may be the formation of $\cdot CR_2\cdot CR'_2\cdot O\cdot$ or $\cdot CR'_2\cdot CR_2\cdot O\cdot$ or both, the actual course being determined by the relative stabilities of the two hydroxyl groups. When the stabilities are about equal, two products are obtained, as, for example, 1 : 1-diethyl*cyclo*hexan-2-one and 1-propionyl-1-ethyl*cyclo*pentane from 1-hydroxydiethylmethyl*cyclo*pentan-1-ol. Hitherto, nothing has been known of the influence of alkyl groups on the stability of hydroxyl groups; since as-dimethyldiethylethylene glycol is transformed into ethyl tert.-amyl ketone, it appears that the hydroxyl group in the neighbourhood of the heavier alkyl group has the greater stability.   C. S.

Syntheses by means of Sodamide. ALBIN HALLER and ÉDOUARD BAUER (*Ann. Chim. Phys.*, 1913, [viii], **28**, 373—414).— A résumé of information on this subject, referring principally to the results recorded in the following Abstracts: 1909, i, 108, 654; 1911, i, 726, and 1912, i, 270.   T. A. H.

A Fourth Modification of Benzophenone. WALTER A. WAHL (*Chem. Zentr.*, 1913, i, 813—814; from *Öfvers. Finska Vetens. Soc. Förhandl.*, 1911, **54**, *A*, 10. Compare A., 1912, ii, 1044).—When benzophenone is melted in a narrow, thin-walled glass tube at 50°, and then plunged into a carbon dioxide-ether mixture, a vitreous mass, is obtained which develops spherulitic groups of fibrous crystals at $-60°$ to $-65°$ which melt at $-51°$. Tammann observed that the speed of crystallisation of stable benzophenone (I) below $-40°$ is so small that this form cannot be produced at such low temperatures at all. The new labile modification (IV) can therefore melt without

passing into the stable form. The other modifications are Tammann's (II) with m. p. 45—48° and Zincke's (III), m. p. 26°.   J. C. W.

Anthracene. III. Derivatives of Anthrone. KURT H. MEYER and ALBERT SANDER (*Annalen*, 1913, **396**, 133—151).—The influence of substituents in position 9 on the desmotropy of anthrone has been further examined. Anthrone itself, even in solution, exists chiefly in the ketonic modification; anthraquinol and its methyl ether, however, are mainly enolic.

On account of its non-fluorescence, insolubility in cold alkalis, and indifference to alcoholic bromine, 9-phenylanthrone exists in the ketonic form. By solution in hot alkali and precipitation by acid in the cold, it is obtained in the form of 9-*phenylanthranol*,

$$C_6H_4 {<}^{C(OH)}_{CPh}{>} C_6H_4,$$
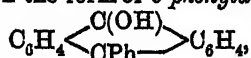
which is sulphur-yellow and yields intensely fluorescent solutions; by keeping or by crystallisation, the anthranol reverts to the anthrone.

The equilibrium of the two modifications of this substance (and also of the following substances) in solution has been determined as follows. An alcoholic solution, about 0·1%, at the ordinary temperature is intensely illuminated by an iron arc and is titrated with $N/10$-alcoholic bromine. Since only the enolic form reacts with bromine and is fluorescent, the disappearance of the fluorescence furnishes a sharp endpoint. The same result is attained by starting with the anthrone or the anthranol, provided that the solution has been kept for a sufficiently long time. By this method it is shown that glacial acetic acid favours the formation of the ketonic modification, that all anthrone derivatives are immediately converted into anthranols by pyridine, that equilibrium is not attained in benzene or chloroform even after prolonged boiling, and that the velocity of transformation in alcohol is very much increased by the addition of concentrated hydrochloric acid and, still more, of sodium acetate.

9-Nitroanthrone, which is readily obtained by the nitration of anthrone in glacial acetic acid by nitric acid, D 1·5, at 60°, is converted into 9-nitroanthranol (Meisenheimer's *aci*-nitroanthrone) by solution in hot alkali and precipitation in the cold by acids. After equilibrium has been established in alcohol, the solution contains 97% of the ketonic form. The end-point is readily detected, since 9-nitroanthranol is yellow, and 9-nitroanthrone is colourless, in solution. 9-Nitroanthrone is converted into 9-*nitroanthranyl acetate*,

$$C_6H_4 {<}^{C(OAc)}_{C(NO_2)}{>} C_6H_4,$$
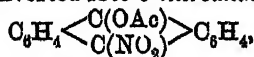
m. p. 182°, citron-yellow leaflets or needles, by acetyl chloride in cold pyridine, and into 9-*nitroanthranyl benzoate*, m. p. 238° (decomp.), amber-yellow prisms, by benzoyl chloride and pyridine on the water-bath.

9-*Anilinoanthrone*, $C_6H_4 {<}^{CO}_{CH(NHPh)}{>} C_6H_4$, m. p. 154—156°, reddening at 146°, faintly yellow needles, prepared from 9-bromo-anthrone and aniline in boiling benzene, is converted by treatment
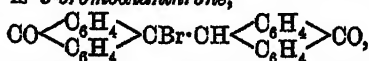
with alcoholic potassium hydroxide and subsequent acidification into 9-*anilinoanthranol*, $C_6H_4\diagdown\diagup\begin{smallmatrix}C(OH)\\C(NHPh)\end{smallmatrix}\diagup\diagdown C_6H_4$, m. p. 155°, reddish-brown crystals, which forms orange-red solutions with intense yellowish-green fluorescence. The alcoholic solution, after several days, contains about 80% of the anthranol. Both forms are converted into anthra-quinol and aniline by boiling dilute acids and alcohol. 9-Anilino-anthrone is converted into 9 *aniloanthrone*, $C_6H_4\diagdown\diagup\begin{smallmatrix}CO\\C(:NPh)\end{smallmatrix}\diagup\diagdown C_6H_4$, m. p. 123—124°, red needles, by alcoholic potassium hydroxide and potassium ferricyanide, and into 9-*anilinoanthranyl benzoate*,

$$C_6H_4\diagdown\diagup\begin{smallmatrix}C(OBz)\\C(NHPh)\end{smallmatrix}\diagup\diagdown C_6H_4,$$
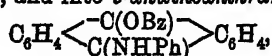
m. p. 226°, yellow crystals, by benzoyl chloride and cold pyridine.

9-β-*Naphthylaminoanthrone*, m. p. 179—180°, yellow needles, 9-β-*naphthylaminoanthranol*, m. p. 187—188°, bluish-black needles, and 9-β-*naphthyliminoanthrone*, m. p. 167—168°, dark red crystals, are prepared by methods similar to the preceding.

With the object of preparing 9-aminoanthrone, a cold solution of 9-bromoanthrone in dry benzene was saturated with ammonia. The product, however, is 9-*bromodianthrone*,

$$CO\diagdown\diagup\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}\diagup\diagdown CBr\cdot CH\diagdown\diagup\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}\diagup\diagdown CO,$$

amber crystals, which, above its m. p., 187°, or by boiling with xylene and copper powder, is converted into dianthrone. 9-Aminoanthrone in a very impure state is produced by reducing benzeneazoanthranol with zinc dust and alcoholic sodium hydroxide in an atmosphere of nitrogen.   C. S.

Experiments on the Determination of the Constitution of Enolic Substances. JOHANNES SCHEIBER and PAUL HEROLD (*Ber.*, 1913, **46**, 1105—1110).—The authors have attempted to apply the use of ozone and subsequent decomposition of the ozonide formed for the determination of the constitution of enolic substances. The advantages claimed for the method are that operations can be carried out at low temperatures and that the addition of ozone, as far as is yet known, takes place without previous structural alteration of the substances investigated.

A solution of benzoylacetone in chloroform was treated with ozone and the ozonide subsequently decomposed by warm water. The cooled solution deposited an almost quantitative amount of benzoic acid, whilst the filtrate, when treated with phenylhydrazine, yielded methyl-glyoxalosazone, m. p. 146° (Harries and Turk, A., 1905, i, 413, give 145°). Neither acetic acid nor carbon dioxide could be detected. Benzoylacetone appears therefore to be enolised according to the formula $OH\cdot CPh:CH\cdot COMe$, which confirms the work of Smedley (T., 1910, **97**, 1486).

Oxalacetone, when similarly treated, gave a 93·5% yield of oxalic acid, from which it follows that enolisation must also have occurred to some extent towards the acetyl group. Although acetic acid could not

be detected, this is confirmed by the fact that phenylhydrazine did not yield pure methylglyoxalosazone.

The ozonide obtained in small quantity from ethyl acetoacetate, when decomposed by water, yielded with phenylhydrazine acetate a precipitate of pure ethyl phenylhydrazonoglyoxylate,

$$NHPh\cdot N\colon CH\cdot CO_2Et,$$

m. p. 128° (Reissert, A., 1895, i, 461, gives 129°; v. Pechmann, 1896, i, 678, finds 130—131°), from which the formula $OH\cdot CMe\colon CH\cdot CO_2Et$ is deduced for the enolised ester.

Ethyl benzoylacetoacetate under similar treatment gave rise to benzoic acid and to the somewhat impure osazone of ethyl diketobutyrate, $CMe(N_2HPh)\cdot C(N_2HPh)\cdot CO_2Et$. Although the benzoic acid formed has not yet been estimated, the enolised form of ethyl benzoylacetoacetate must possess mainly the configuration

$$OH\cdot CPh\colon C(COMe)\cdot CO_2Et.$$
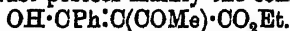
Diacetylbenzoylmethane, m. p. 34°, similarly yielded benzoic acid mixed•with small quantities of a substance which could not be identified with certainty, whilst, after removal of benzoic acid, the bisphenyl-hydrazone of triketopentane, m. p. 155° (Sachs and Barschall, A., 1901, i, 670, give 156°), was isolated by means of phenylhydrazine. The authors conclude that the enolised form of diacetylbenzoylmethane consists mainly of the α-form, $CPh(OH){=}C{<}^{COCH_3}_{COCH_3}$, probably mixed with small amounts of the β-variety, $CMe(OH){=}C{<}^{COCH_3}_{CO\cdot C_6H_5}.$

H. W.

Phthalylglycyl Derivatives of Acetylacetone, Benzoylacetone, and Ethyl Cyanoacetate. JOHANNES SCHEIBER [with K. KLOPPE and K. SCHNABEL] (*Ber.*, 1913, 46, 1100—1105).—The author has extended his work on the condensation of ethyl sodioacetoacetate with phthalylglycyl chloride (A., 1909, i, 390).
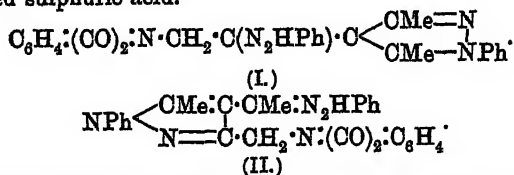
The sodium derivative of acetylacetone reacts readily with phthalyl-glycyl chloride in the presence of ether or benzene. The main product of the reaction is *bisphthalylgylcylcylacetylacetone*, smaller quantities of *C-phthalylglycylacetylacetone* and *o-phthalylglycylacetylacetone* being also formed. The latter substance is, however, mainly formed when the silver derivative of acetylacetone is substituted for the sodium derivative. If the reaction is carried out in boiling benzene solution, *phthalylglycyl anhydride* is also obtained.

Bisphthalylglycylacetylacetone,

$$C_6H_4{<}^{CO}_{CO}{>}N\cdot CH_2\cdot CO\cdot O\cdot CMe\colon C(COMe)\cdot CO\cdot CH_2\cdot N{<}^{CO}_{CO}{>}C_6H_4,$$
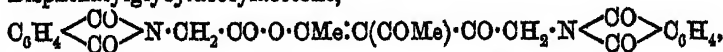
has a variable m. p., probably due to partial enolisation. Thus, a product, m. p. 182° (highest observed m. p.), after recrystallisation from glacial acetic acid had m. p. 168°. Cold sodium ethoxide converts it into *C*-phthalylglycylacetylacetone. With aniline it yields *phthalylglycyl-acetylacetone anilide*, $C_6H_4\colon(CO)_2\colon N\cdot CH_2\cdot CO\cdot C(COMe)\colon CMe\cdot NHPh$, yellow needles, m. p. 172°. Phenylhydrazine converts it into *phthalyl-glycylacetylacetonepyrazolephenylhydrazone* (formula I or II), lemon-yellow leaflets, m. p. 192°, the same substance being obtained from the

above anilide or from C-phthalylglycylacetylacetone. It is not decomposed by sodium hydroxide, does not reduce Fehling's solution, and gives a blue coloration with ferric chloride when dissolved in concentrated sulphuric acid.

$$C_6H_4{:}(CO)_2{:}N{\cdot}CH_2{\cdot}C(N_2HPh){\cdot}C{<}^{OMe=\!\!N}_{OMe-\!\!NPh}{\cdot}$$

(I.)

$$NPh{<}^{OMe{:}C{\cdot}OMe{:}N_2HPh}_{N=\!\!\!=\!\!C{\cdot}CH_2{\cdot}N{:}(CO)_2{:}C_6H_4}{\cdot}$$

(II.)

C-Phthalylglycylacetylacetone, m. p. 124°, is soluble in aqueous sodium hydroxide without decomposition, and gives an immediate blood-red coloration with alcoholic ferric chloride.

O-Phthalylglycylacetylacetone, m. p. 107°, is insoluble in aqueous sodium hydroxide, and yields a red coloration with ferric chloride after some time. It is decomposed by a solution of phenylhydrazine in glacial acetic acid with formation of *phthalylglycylphenylhydrazide*, $C_6H_4{:}(CO)_2{:}N{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}NHPh$, m. p. 192°, which was also prepared from phthalylglycyl chloride and phenylhydrazine. When, however, the free acid was heated with phenylhydrazine in dilute acetic acid solution, the main product was anilinophthalimide, $C_6H_4{:}(CO)_2{:}N{\cdot}NHPh$, m. p. 179°.

Phthalylglycyl anhydride, $C_{20}H_{12}O_7N_2$, white needles, m. p. 242°, is transformed by phenylhydrazine into phthalylglycylphenylhydrazide, and by aniline into phthalylglycylanilide, m. p. 231—232°. The latter substance was also obtained from phthalylglycyl chloride and aniline.

The action of phthalylglycyl chloride on the sodium derivative of benzoylacetone yields *bisphthalylglycylbenzoylacetone* and O-*phthalylglycylbenzoylacetone*. The former, m. p. 151°, gradually gives a red coloration with ferric chloride in alcoholic solution, and is converted by cold sodium alkoxide into O-*phthalylglycylbenzoylacetone*, m. p. 135°. The latter immediately gives an intense red coloration with ferric chloride.

O-Phthalylglycylbenzoylacetone, m. p. 147—148°, gives no coloration with ferric chloride, and is insoluble in sodium hydroxide. Phenylhydrazine eliminates the phthalylglycyl radicle.

With ethyl sodiocyanoacetate, phthalylglycyl chloride yields practically solely *ethyl phthalylglycylcyanoacetate*, long needles, m. p. 149°. The ester is immediately soluble in alkali and alkali carbonate solutions, and gives an immediate intense red coloration with ferric chloride. An alcoholic solution of phenylhydrazine converts it into phthalylglycylphenylhydrazide. In glacial acetic acid solution at the ordinary temperature, however, phenylhydrazine converts it into a *substance*, $C_{21}H_{20}O_5N_4$, m. p. 156°, which is probably an additive product. It is soluble in sodium hydroxide, does not give Bülow's reaction, and reduces Fehling's solution in the cold. Concentrated sulphuric acid regenerates the ester.   H. W.

Action of Hydrochloric Acid on p-Benzoquinonesulphonic Acid. ALPHONSE SEYEWETZ (*Compt. rend.*, 1913, **156**, 901—903).— Concentrated hydrochloric acid acting on sodium p-benzoquinone-

sulphonate at temperatures below 20° yields after twelve hours a crystalline mass of *sodium chloroquinolsulphonate*, $C_6H_2Cl(OH)_2 \cdot SO_3Na$, white needles, soluble in water, instantly reducing silver nitrate. On oxidation it is converted into chloro-*p*-benzoquinonesulphonic acid.

If the reaction takes place at above 20°, the products are chloroquinol and 2 : 6-dichloroquinol. W. G.

Action of Nitrous Acid on Dianilino-*p*-benzoquinoneanil. CONSTANTIN I. ISTRATI and M. A. MIHAILESCU (*Bull. Acad. Sci. Roumaine*, 1912/3, 1, 25—29. Compare Istrati, A., 1903, i, 82).—When an excess of sodium nitrite is added to a solution of dianilino-*p*-benzoquinoneanil in cold glacial acetic acid, a number of *products* are obtained, of which three, m. p. 209°, 248° and 286° respectively, have been isolated. The first of these separates from toluene in brilliant red leaflets. It is not attacked by boiling solutions of alkali hydroxides. It dissolves in concentrated sulphuric acid and in fuming nitric acid, but is precipitated unchanged when these solutions are diluted with water. It gives Liebermann's reaction, but the presence of a nitro-group could not be established. The formula,

$$\text{NO·NPh·C} {\overset{\text{CH}——\text{CO}}{\underset{\text{C(NPh)·CH}}{\bigg\langle}}} \text{C·N:C} {\overset{\text{CH:CH}}{\underset{\text{CH:CH}}{\bigg\langle}}} \text{CO},$$

is assigned to it, the dinitrosoamine first formed undergoing partial rearrangement with the formation of the oxime of a substituted *p*-benzoquinoneimide, from which the *p*-benzoquinone is formed by elimination of hydroxylamine. H. W.

Metaquinonoids. RICHARD MEYER (*Ber.*, 1913, 46, 1220).— Stark and Garben (this vol., i, 361) relying on the earlier work of Meyer and Desamari (A., 1908, i, 658) included Liebermann and Dittler's tribromoresoquinone as a substance of metaquinonoid type. Later experiments of these authors, however, had already shown that the compound was a bimolecular keto-bromide, $C_{12}H_2O_4Br_6$ (A., 1909, i, 241, 657). J. C. W.

Preparation of Anthraquinone from Anthracene. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 256623).—Anthraquinone is obtained in 94—96% yield when an intimate mixture of anthracene, glass wool, or asbestos powder, and a metal or metallic oxide (such as zinc dust or lead oxide) is carefully treated with nitric acid fumes at 75—100° for about nine hours; the temperature is then slowly raised to 280°, when the anthraquinone sublimes in long, yellow needles. F. M. G. M.

Preparation of Chlorinated Anthraquinones and Anthracenes. H. SCHILLING (*Ber.*, 1913, 46, 1066—1069).—Starting from 1- and 2-chloroanthraquinone and from 1 : 5- and 1 : 8-dichloroanthraquinone, the author has prepared a number of the higher chlorinated anthraquinones by converting them into the corresponding chloroanthraquinonesulphonic acids and replacing the sulphonic acid with chlorine by treatment of the potassium salts of the sulphonic acids with chlorine in aqueous solution at 100°. The sulphonation

was carried out by heating the chloroanthraquinones with sulphuric acid containing 20% of anhydride for four hours at 150—160°, both alone and in the presence of mercurous sulphate. Although the position of the sulphonic acid groups has not been definitely established, it is assumed from the results of Schmidt (A., 1904, i, 256) and Iljinsky (A., 1904, i, 176) that in the presence of the mercurous salt the sulphonic acid group takes up the α-position, whilst if no catalyst is employed the group enters the β-position.

With sulphuric acid alone monosulphonic acids are obtained. In the presence of mercurous sulphate 1-chloro- and the two dichloroanthraquinones yield disulphonic acids, whilst 2-chloroanthraquinone forms a monosulphonic acid. In addition to the disulphonic acid the 1:5-dichloro-compound also yields a monosulphonic acid.

The potassium salts of the chloroanthraquinonesulphonic acids are colourless or pale yellow, and are sparingly soluble in water.

The chloroanthraquinones are converted by reduction with zinc dust and ammonia into the corresponding chloroanthracenes, of which the monochloro-compounds form colourless, strongly, fluorescent leaflets or needles, whereas the di-, tri-, and tetra-chloro-derivatives crystallise in yellow needles.

In the following, (a) denotes sulphonation in the absence, (b) in the presence, of mercurous sulphate.

1-Chloroanthraquinone yields (a) 1-*chloroanthraquinonesulphonic acid* and (b) 1-*chloroanthraquinone-αα-disulphonic acid*; αβ-*dichloro*- (m. p. 166—168°) and ααα-*trichloro-anthraquinones*, m. p. 165—168°, which are reduced to αβ-*dichloro*- (m. p. 130—135°) and ααα-*trichloroanthracene* (m. p. 133—135°).

2-Chloroanthraquinone gives rise to (a) 2-*chloroanthraquinone-β*- and (b) -α-*sulphonic acids*; ββ- and αβ-*dichloroanthraquinones* have m. p. 284—285° and 278—280° respectively, and yield ββ- and αβ-*dichloroanthracenes*, m. p. 216° and 155—160°.

1:5-Dichloroanthraquinone gives rise to (a) 1:5-*dichloroanthraquinone-β-sulphonic acid* and (b) 1:5-*dichloroanthraquinone-α-sulphonic* and -αα-*disulphonic acids*; 1:5-β- (m. p. 230—235°) and 1:5-α-*trichloroanthraquinone*, m. p. 256°, and 1:5:4:8-*tetrachloroanthraquinone*, m. p. 339°; 1:5-β-*trichloroanthracene* has m. p. 170—175°, the 1:5:4:8-*tetrachloro*-compound, m. p. 275° or 285—286°, and the 1:5:α-*trichloro*-compound, m. p. 270—275°.

1:8-Dichloroanthracene yields (a) 1:8-*dichloroanthraquinone-β-sulphonic acid* and 1:8-*dichloroanthraquinone-αα-disulphonic acid*; 1:8:β-*trichloroanthraquinone*, m. p. 295—300°, and 1:8:β-*trichloroanthracene*, m. p. 185—190°.

1-*Chloroanthracene* has m. p. 81—82°, 2-*chloroanthracene*, m. p. 215°, 1:5-*dichloroanthracene*, m. p. 185°, and 1:8-*dichloroanthracene*, m. p. 156°.

F. B.

Preparation of Selenocyanates of the Anthraquinone Series.

FARBENFABRIKEN VORM FRIEDR. BAYER & Co (D.R.-P. 256667).—When the anthraquinone diazoselenocyanates are carefully heated (preferably in the presence of copper or cuprous salts) nitrogen

is eliminated and the selenocyanate group enters the ring :
$$C_{14}H_7O_2 \cdot N_2 \cdot SeCN = N_2 + C_{14}H_7O_2 \cdot SeCN.$$
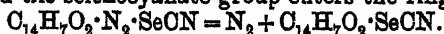
1-*Selenocyanoanthraquinone*, yellowish-red needles, m. p. 249°, is obtained when aminoanthraquinone (2·2 parts) is diazotised in concentrated sulphuric acid with nitrosyl sulphate, ice added, and the precipitated diazonium sulphate collected, dissolved in water, and treated with an aqueous solution of potassium selenocyanate (1·5 parts); the precipitated red *diazoanthraquinone selenocyanate* when warmed is converted into 1-selenocyanoanthraquinone, which is purified by crystallisation from nitrobenzene. *Potassium 1-selenocyanoanthraquinone-5-sulphonate* is prepared in a similar manner from sodium 1-aminoanthraquinone-5-sulphonate.　　　　　　　　　　　　　F. M. G. M.

Preparation of 2-Anthraquinone Sulphide. Irma Ullmann-Goldberg (D.R.-P. 255591).—2-*Dianthraquinonyl sulphide*, orange-yellow prisms, m. p. 275—276°, is obtained when 2-chloroanthraquinone is boiled for six hours with an equal weight of potassium xanthate and 10 parts of amyl alcohol.　　　　　　　　　F. M. G. M.

Action of Colloidal Metallic Hydroxides on Hydroxyanthraquinones. R. Haller (*Farber-Zeit.*, 1912, **23**, 489—492, 523—528).—A description of the preparation of colloidal solutions of aluminium, chromium, and ferric hydroxides, and of the complex salts : $Al_2(SO_4)_2(OH)_2$, $Al_2(SO_4)_3(OAc)_3$, $Al_2(SO_4)(OAc)_4$,
$$Al_2(SO_4)(OH)_2(OAc)_2,$$
$Al_2(OAc)_6$, $Al_2(OAc)_4(OH)_2$, and $Al_2(OAc)_2(OH)_4$; these were combined with alizarin, purpurin, anthrapurpurin, flavopurpurin, and alizarin-orange, and the physical and chemical properties of the *compounds* so obtained are comparatively tabulated with the normal iron, aluminium, and chromium salts.

The following properties were studied, absorption spectra, together with their behaviour in the presence of hydrochloric acid, ammonium hydroxide, calcium chloride, sodium chloride, sodium hydrogen phosphate, and absolute alcohol.　　　　　　　　　　　　F. M. G. M.

Bupleurol or Dihydronerol Constitution. II. Luigi Francesconi and E. Sernagiotto (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 148—154. Compare this vol., i, 283).—Reasons are advanced showing that bupleurol probably has the structure : $CHMe_2 \cdot [CH_2]_3 \cdot C(:CH_2) \cdot CH_2 \cdot CH_2 \cdot OH.$　　　　R. V. S.

The Autoxidation of Turpentine. Arnold Blumann and Otto Zeitschel (*Ber.*, 1913, **46**, 1178—1198).—On distilling a resinified Grecian turpentine in steam, the less volatile portions were found to respond to tests for aldehydes (compare Schiff, A., 1883, 1141). An oil, $C_{10}H_{14}O$, was obtained on fractionation, but it was stable towards alkalis, did not readily yield an acid on oxidation, or a secondary alcohol with the Grignard reagent, neither would it undergo condensations. It was therefore considered to be a ketone with pseudo-aldehydic properties, like Wallach's *iso*propyl-Δ^2-hexenone (A., 1908, i, 425). Further investigations showed that it was unsaturated, and that it gave a saturated secondary alcohol with sodium

and moist ether, and a saturated ketone by Paal's reduction. It was completely identified with Kerschbaum's verbenone (A., 1900, i, 353), and its constitution was established, the chief evidence being that it gave pinononic acid on oxidation with permanganate (experiments by F. MEISTER), and that hydrolysis with dilute sulphuric acid resulted in the formation of acetone and a methyl*cyclo*hexenone, which gave γ-acetobutyric acid on oxidation.

3-Methyl*cyclo*-Δ²-hexene-1-one.   γ-Acetobutyric acid.

Its rotation was stated by Kerschbaum to be + 66°, but it is really more by 180°. The *l*-modification was also obtained from French turpentine. Besides verbenone, the crude product contained alcoholic substances, evidence of the existence of verbenol being obtained, although the substance could not be completely purified.

The fact that the unsaturated linking of pinene is preserved after autoxidation seems contradictory, but it is assumed that the addition of water at this point precedes oxidation, and that after the latter process has occurred at the neighbouring –CH₂-group, the water is again eliminated.

From 900 grams of the less volatile constituents of Grecian turpentine which had been exposed to air for six months, 146 grams were collected at 105—107°/5 mm. *d*-Verbenone, $C_{10}H_{14}O$, was separated from this by a neutral sulphite solution with sodium hydrogen carbonate (compare Tiemann, A., 1899, i, 247), or as the semicarbazone, in the form of a colourless oil, which soon became yellow in the light. It had b. p. 227—228°, or 100°/16 mm., m. p. 6·5°, D^{15} 0·981, D^{20} 0·9780 $[a]_D$ + 249·62°, $[a]_D$ in alcohol + 229·60°, $[a]_D$ in benzene + 245·70°, n_D^{18} 1·49928. It formed an *oxime*, $C_{10}H_{14}\cdot NOH$, m. p. 115°, was scarcely affected by hydrogen chloride in carbon disulphide or ether, or by acetic anhydride, but it absorbed hydrogen chloride with partial decomposition in glacial acetic acid. On reduction with sodium in moist ether, it yielded *dihydro*-d-*verbenol*, $C_{10}H_{18}O$, in silky needles with the celery-like smell of verbenone, m. p. 58°, b. p. 218°, a_D + 1°30′ (10% alcoholic solution). The *acetate*, D^{15} 0·9926, a_D – 0·50° (25 mm.), and the *phthalate*, $C_{18}H_{22}O_4$, m. p. 127—129°, were prepared. On

oxidation it yielded *dihydro-d-verbenone*, $C_{10}H_{16}O$, which was also obtained by reduction of verbenone with colloidal palladium and hydrogen as an oil, b. p. 222°, D^{15} 0·9685, D^{18} 0·966, D^{20} 0·9642, $[a]_D$ +52·19°, n_D 1·47535. The *semicarbazone*, m. p. 220—221°, the *oxime*, m. p. 77—78°, and the *benzylidene* compound, m. p. 152—153°, or 103—104° after three months, were obtained. Verbenone was also treated with magnesium methiodide, when the lowest fraction of the product was found to be an inactive hydrocarbon, *methylverbenene*, $C_{11}H_{16}$. The pure substance had b. p. 49°/8 mm., 175—176°/771 mm., D^{15} 0·876, D^{20} 0·872, n_D^{20} 1·4969.

One kilogram of French turpentine was also exposed to air for three months, and 370 grams of less volatile products were fractionated, yielding 41·5 grams at 90—100°/12 mm. By means of neutral sulphite, 18 grams of l-*verbenone* were obtained, having a lower rotation than the isomeride, $[a]_D$ – 126·84°, D^{15} 0 980, n_D 1·4994, and forming a *semicarbazone*, m. p. 185—190°. The semicarbazone from inactive verbenone had m. p. 180—181°.

The alcohol present in the residue which remained after shaking the high fraction with sulphite was isolated by means of benzoyl chloride in pyridine. The benzoate, D^{15} 1·048, gave an oil on hydrolysis, which solidified in a freezing mixture to a mass of large leaflets. After pressing out the impurities the purified d-*verbenol*, $C_{10}H_{16}O$, had the constants, b. p. 216—218°, with elimination of water, D^{15} 0·9742, D^{18} 0 9722, D^{20} 0·9702, $[a]_D$ +132·30°, n_D^{20} 1·4890. No solid derivatives could be obtained, but the alcohol gave verbenone with chromic acid, and pinononic acid with permanganate. When the crude or pure substance was heated with acetic anhydride, water was easily removed and l-*verbenene*, $C_{10}H_{14}$, was obtained, b. p. 159—160°, D^{15} 0·8852, D^{20} 0·8822, a_D^{19} – 74·90° (100 mm.), n_D^{20} 1·49855. On the other hand, phosphoric oxide or zinc chloride yielded a hydrocarbon which was proved to be p-cymene, since it gave p-hydroxyisopropylbenzoic acid on warming with permanganate. The residue from l-verbenone was treated as above, but, although l-verbenol was found, it was still more difficult to purify it.   J. C. W.

Synthetic β-Glucosides of the Terpene Alcohols. JULIO HAMALAINEN (*Biochem. Zeitsch.*, 1913, **49**, 398—412).—The alcohols were shaken in ethereal solution with acetobromoglucose and silver carbonate, which were added in portions alternately. The glucosides were then obtained from the acetyl compounds thus produced by hydrolysis with barium hydroxide. The following substances were obtained: d-*Citronellol-tetra-acetyl*-d-*glucoside*, $C_{24}H_{88}O_{11}$, m. p. 30° (corr.), white needles from dilute alcohol. d-*Citronellol*-d-*glucoside*, $C_{16}H_{80}O_6$, a viscid syrup, with $[a]_D^{20}$ – 28·59°; it is hydrolysed by emulsin. cyclo*Hexanol-tetra-acetyl*-d-*glucoside*, $C_{20}H_{80}O_{10}$, m. p. 119—120° (corr.), and cyclo*hexanol*-d-*glucoside*, $C_{12}H_{22}O_6$, m. p. 133—135° (corr.) (without water of crystallisation), with $[a]_D^{20}$ – 42·52°. The substance with water of crystallisation has m. p. 128·5—129·5° (corr.); it is not very readily hydrolysed with emulsin. *Terpineol-32°-tetra-acetyl*-d-*glucoside*, $C_{24}H_{36}O_{10}$, m. p. 114—116°. *Terpineol-32°*-d-*glucoside*, $C_{16}H_{28}O_6$, sinters at 50°, m. p. 90°, with $[a]_D^{20}$ – 10·94° when

anhydrous, and has a bitter taste. The form with $1H_2O$ has m. p. 80·5—82·5° (corr.). The glucoside is not readily hydrolysed by emulsin. *Terpineol*-35°-*tetra-acetyl*-d-*glucoside*, $C_{24}H_{86}O_{10}$, m. p. 130—132° (corr.). *Terpineol*-35°-d-*glucoside*, $C_{16}H_{28}O_6$, sinters at 100°, m. p. 110° (water free), with $[a]_D^{20} - 5·88°$; it has a bitter taste; with water of crystallisation it melts at 106—108° (corr.); it is slowly hydrolysed by emulsin. d-*Dihydrocarveol-tetra-acetyl*-d-*glucoside*, $C_{24}H_{86}O_{10}$, m. p. 155—156° (corr.). d-*Dihydrocarveol*-d *glucoside*, $C_{16}H_{28}O_6$, m. p. (with water of crystallisation) 164—165° (corr.), with $[a]_D^{20} + 36·52°$. It is only sparingly soluble in water, and is hydrolysed readily by emulsin. cis-*Terpin-tetra-acetyl*-d-*monoglucoside*, $C_{24}H_{88}O_{11}$, m. p. 129—139° (corr.). cis-*Terpin*-d-*monoglucoside*, $C_{16}H_{80}O_7, H_2O$, m. p. 143—149° (corr.), with $[a]_D^{20} - 11·09°$, is not readily hydrolysed by emulsin.   S. B. S.

Synthesis of Alkyl Glucosides by means of Emulsin, β-Phenylethyl Glucoside, and β-Cinnamyl Glucoside. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1913, 156, 827—829; *J. Pharm. Chim.*, 1913, [vii], 7, 335—340).—The authors have prepared two other glucosides by their usual method (compare A., 1912, i, 672).

β-*Phenylethyl glucoside*, $C_6H_{11}O_6 \cdot CH_2 \cdot CH_2Ph$, crystallises in colourless needles, having a bitter taste. It has $[a]_D - 23·92°$, and reduces Fehling's solution.

β-*Cinnamyl glucoside*, $C_6H_{11}O_6 \cdot CH_2 \cdot CH:CHPh$, crystallises in colourless needles, $[a]_D - 41·12°$, and having only a slight reducing action. Both of these glucosides are readily hydrolysed by emulsin in aqueous solution.   W. G.

Synthesis of Alkyl Galactosides by means of Emulsin. β-Methyl Galactoside and β-Allyl Galactoside. ÉMILE BOUR-QUELOT and MARC BRIDEL (*Compt. rend*, 1913, 156, 1104—1106[*]).—The two galactosides were prepared in the usual way by the action of emulsin on solutions of galactose in the respective alcohols. After evaporating off the excess of alcohol under reduced pressure, the unaltered galactose was destroyed by fermentation with bottom yeast in the presence of dextrose.

β-*Allyl galactoside* crystallises in colorless needles, $[a]_D - 12·5°$, and, like the methyl galactoside, it is readily hydrolysed by emulsin in aqueous solution.   W. G.

Rhamnoxanthin from Rhamnus cathartica and Frangulin from Rhamnus frangula. N. KRASOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 188—193. Compare A., 1909, ii, 174).—Examination of the two glucosides, rhamnoxanthin, and frangulin, and of their derivatives and products of hydrolysis indicates their identity. The name frangulin is suggested for retention.   T. H. P.

Preparation of the Active Principle of Apocynum. FAR-BENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 255537. Compare T., 1909, 95, 734).—The boiling carbon tetrachloride extract of the rhizome of *Apocynum cannabinum* furnished a *compound*, glistening prisms, m. p. 135—140°, with an extremely bitter taste, and contain-

* and *J. Pharm. Chim.*, 1913, [vii], 7, 444—448.

ing $C = 63\cdot5\%$ and $H = 8\cdot4\%$ (compare Finnemore, T., 1908, **93**, 1513; P., 1909, **25**, 77). F. M. G. M.

The Blue Pigment from Crenilabrus pavo. RICHARD VON ZEYNEK (*Monatsh.*, 1913, **34**, 535—551. Compare A., 1902, i, 168). —A fuller account of the blue protein substance present in the fins, scales, and skin of *Crenilabrus pavo*. The fins, which are the best source of the substance, are extracted with acetone and ether successively, which remove a yellow *substance*, microscopic needles; this is easily soluble in chloroform, giving a solution which, on treatment with acetic anhydride and a drop of concentrated sulphuric acid, assumes a deep red colour, shortly changing to a bluish-green. After the above treatment, the fins are extracted with water, which dissolves out the coloured substance; this is purified by repeated precipitation by ammonium sulphate, and obtained as an amorphous solid. The optical properties of the substance have been re-investigated. The addition of magnesium sulphate, ammonium chloride, or sodium chloride causes the substance to separate slowly from its aqueous solution, and it is precipitated by the ordinary alkaloid reagents; its neutral solution coagulates at 75—77°, precipitating green flocks. The colour is only slowly bleached by hydrogen peroxide and hydrazine hydrate, but it is very sensitive towards acids, which evidently cause decomposition, as subsequent neutralisation fails to restore the original colour.

D. F. T.

Chlorophyll. XXI. Introduction of Magnesium into Chlorophyll Derivatives. RICHARD WILLSTÄTTER and LENNART FORSÉN (*Annalen*, 1913, **396**, 180—193).—It has previously been shown that metals, such as copper, iron, and zinc, can easily be introduced into derivatives of chlorophyll, such as the phæophorbides, phytochlorins, phytorhodins, and the various porphyrins, producing substances which are characterised by their stability in acid or alkaline media. Also derivatives of the phytochlorins and the phytorhodins have been prepared containing barium or potassium, and characterised by their instability towards acids. The magnesium derivatives are intermediate between these two extremes in their degree of stability. The present paper deals with the important problem of the methods whereby magnesium can be introduced into chlorophyll derivatives which do not contain a metallic constituent.

Two methods are described: heating the chlorophyll derivative with methyl-alcoholic potassium hydroxide and magnesium oxide under pressure, and secondly, treating it with an excess of ethereal magnesium methyl iodide.

Thus by heating phytochlorin-*e* (violet modification) with concentrated methyl-alcoholic potassium hydroxide and magnesium oxide in a silver autoclave at 180°, isolating the resulting potassium salt, and acidifying it with sodium dihydrogen phosphate, a new phyllin, called *cyanophyllin*, $C_{33}H_{34}O_4N_4Mg,Et_2O$, is obtained; it is a greenish-blue substance, characterised by the colour and fluorescence of its solutions and by its extraordinary instability, whereby the corresponding porphyrin is produced.

At 200° under similar conditions, phytochlorin-*e* is converted into a second phyllin, called *erythrophyllin*, $C_{33}H_{34}O_4N_4Mg$, which forms a red, fluorescent solution in ether. Still under the same conditions, phytochlorin-*e* at 220° is converted into phyllophyllin, $C_{32}H_{34}O_2N_4Mg$, which has previously been analysed only in the form of its salts on account of its instability. Phyllophyllin forms a bluish-red fluorescent ethereal solution, and readily loses its magnesium, yielding phylloporphyrin.

By treatment with magnesium methyl iodide (1 or 2 mols.) in ether, phæophytin-*a* yields precipitates containing magnesium and iodine, from which, however, the phæophytin is regenerated by treatment with water or other reagents. With an excess of magnesium methyl iodide (8 mols.), chlorophyll yields a substance from which unchanged chlorophyll is regenerated by treatment with sodium dihydrogen phosphate. In a similar manner the precipitate obtained from phæophytin-*a* and magnesium methyl iodide (8 mols.) yields, when rapidly treated with 10% sodium dihydrogen phosphate, pure chlorophyll-*a* identical with the substance prepared from natural sources.

In a similar manner, all porphyrins can be converted into the corresponding phyllins; thus phylloporphyrin methyl ester and magnesium methyl iodide in boiling ether yield a substance by the decomposition of which by sodium dihydrogen phosphate the methyl ester of phyllophyllin, $C_{33}H_{36}O_2N_4Mg$, is obtained in large, rhombic leaflets.

C. S.

[**Action of Sodium Methoxide on Bilirubic Acid, Bilirubin, and Hemibilirubin.**] OSKAR PILOTY (*Ber.*, 1913, **46**, 1000—1001).— Polemical (compare Fischer and Róse, A., 1912, i, 575; this vol., i, 382; also Piloty and Thannhauser, A., 1912, i, 736, 925). Bilic and bilirubic acids are the same substance; further, *iso*phonopyrrolecarboxylic acid is identical with the *iso*phonopyrrolecarboxylic acid of Fischer and Bartholomäus (A., 1912, i, 493), whilst dehydrobilic acid represents Fischer's xanthopyrrolecarboxylic acid or xanthobilirubic acid. The former name is to be preferred in each instance.

E. F. A.

The **Action of Hydrogen Peroxide on Hippomelanin.** JENNY ADLER-HERZMARK (*Biochem. Zeitsch.* 1913, **49**, 130—136).— Hippomelanin, obtained from melanotic lymph glands of a horse, dissolves in hydrogen peroxide when treated by the method of Rona and Riesser. About two-thirds of the nitrogen is thereby obtained in the form of ammonia. Part of the substance is converted into a product of the nature of melanic acid, which has been obtained from melanin by other methods. This product is slightly soluble in water, and is obtained in solution by the above-mentioned treatment in the form of an ammonium salt, from which the free acid can be precipitated by mineral acids, and from which an insoluble mercury salt can be obtained. No evidence could be obtained of the formation of guanidine or other basic organic substances.
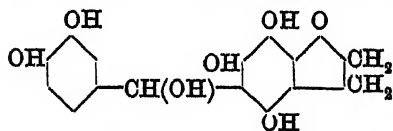
S. B. S.

Furoylformic Acid and Furylglycollic Acid. EMIL FISCHER and FRITZ BRAUNS (*Ber.*, 1913, **46**, 892—896).—The similarity of pyromucic acid to benzoic acid extends even to the conversion through the chloride and cyanide into the corresponding ketonic acid.

Pyromucyl chloride, obtained from pyromucic acid and thionyl chloride, was treated in cooled ethereal solution with hydrogen cyanide and pyridine; the resultant oil was separated by distillation into a distillate of *furoyl cyanide*, hexagonal tablets, m. p. 25°, b. p. 32°/ 0·15 mm., and a residue of pyromucic anhydride. Furoyl cyanide is converted by dilute sodium hydroxide, or slowly by moist ethereal solution, largely into pyromucic acid. When kept with hydrochloric acid (D 1·19) for twenty-four hours, *furoylformic acid*, $C_4H_3O\cdot CO\cdot CO_2H$, is formed, which separates in colourless, microscopic needles, m. p. 94—95°, when the ethereal extract is treated with light petroleum; *silver* salt, amorphous; *phenylhydrazone*, m. p. near 154° (decomp.). The reduction of furoylformic acid by shaking with sodium amalgam and water yields *furylglycollic acid*, $C_4H_3O\cdot CH(OH)\cdot CO_2H$, m. p. indefinite at 114° (decomp.); the *calcium*, *silver*, and *lead* salts were prepared. Furoylformic acid thus shows marked similarity to benzoylformic acid.

D. F. T.

Hydroxycatechin and Catechincarboxylic Acids. MAXIMILIAN NIERENSTEIN (*Annalen*, 1913, **396**, 194—200).—*Hydroxycatechin* (annexed formula), m. p. 284—285° (decomp.), prepared by the reductive acetylation of catechone by acetic anhydride and zinc dust and hydrolysis of the product, crystallises in yellow needles and forms a colourless *hexamethyl ether*, m. p. 102°, by treatment with diazomethane.

The yellow colour of hydroxycatechin, as also the red colour of 1 : 2 : 7 : 8-tetrahydroxydiphenylene oxide, is attributed to the influence of the hydroxyl group in the peri-position to the oxygen atom of the furan ring. Consequently, the presence of the more strongly acidic carboxyl group in the place of the peri-hydroxyl group should produce a still more intensely coloured catechincarboxylic acid. The interaction of catechin, carbon tetrachloride, and aqueous potassium hydroxide, however, leads to the formation of a colourless *catechincarboxylic acid*, m. p. 274—277° (decomp.), needles, which has the constitution $CO_2H\cdot C_6H_2(OH)_2\cdot CH(OH)\cdot C_6H(OH)_2{<}^{O}_{CH_2}{>}CH_2$, since the *methyl catechincarboxylate pentamethyl ether*, $C_{22}H_{26}O_8$, m. p. 92°, obtained from it by the action of diazomethane, yields hemipinic acid by oxidation with alkaline potassium permanganate.

The catechincarboxylic acid has been resolved by means of its strychnine salts into the optically active components. l-*Catechincarboxylic acid* crystallises in small needles and has m. p. 270—273° (decomp.), and $[a]_D^{18} - 68\cdot 22°$ in alcohol; the d-*acid*, small needles, has m. p. 273° (decomp.) and $[a]_D^{18} + 76\cdot 4°$ in alcohol. C. S.

Adrenaline from the Whale. EDWARD R. WEIDLEIN (*J. Ind. Eng. Chem*, 1912, **4**, 636—645).—The suprarenal glands of the whale are found to be about 500 times larger than those of sheep and fifty times larger than those obtained from cattle.

From the tabulated results of numerous experiments the conclusion is drawn that glands preserved in chloroform yield about 0·2% pure adrenaline (m. p. 212°, $[a]_D^{25}$ −52·00°) after preservation during six to nine months, the loss during purification amounting to 13·8%. Pure adrenaline gives a marked increase in blood pressure (as shown by curves) without a subsequent depressant action, this latter effect being considered to be due to impurities, proteins (such as lecithin and phosphates) present in the glands, and to decomposition products which are formed by oxidation on keeping for even a a short time in aqueous solution.

The commercial adrenaline used for comparison gave the secondary depressant action until purified, although declared to be the best on the market.

The extraction and purification of the active suparenal principle from the whale, cattle, sheep, and pigs is described, and it is demonstrated to be identical from each source.   F. M. G. M.

Berberine. MARTIN FREUND (*Annalen*, 1913, **397**, 1—30).—A general discussion of the results of researches on dihydroberberine derivatives (compare following abstracts), one of the most important being the conversion of berberine into hydrastinine by a smooth and practicable method.   C. S.

Derivatives of Benzyldihydroberberine. MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1913, **397**, 30—52).—Benzyldihydroberberine (Freund and Beck, A., 1905, i, 151) yields the stannichloride of *benzyltetrahydroberberine*,

$$C_6H_2(OMe)_2\underset{CH(CH_2Ph)\cdot N\cdot CH_2\cdot CH_2}{\overset{CH_2\text{———}CH\text{———}}{\Big\langle}}C_6H_2\text{:}CH_2O_2,$$
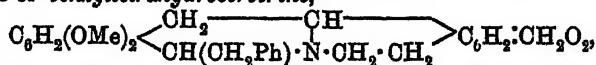
m. p. 163—165°, pale yellow, rhombic plates (*hydrochloride*, white needles ; *sulphate*, decomp. 227° ; *nitrate*, decomp. 175°), by reduction with stannous chloride and boiling 96% alcohol and hydrochloric acid, D 1·19. A second base is not formed, but when benzyldihydroberberine, dissolved in alcohol and 30% sulphuric acid, is reduced at a lead cathode at 50—60° (current-density at the cathode 0·06 ampere per sq. cm.), benzyltetrahydroberberine is produced, together with an *isomeride*, $C_{27}H_{27}O_4N$, m. p. 126°, a grey, crystalline powder, which is called *ψ-benzyltetrahydroberberine.* With methyl iodide at 100° it forms a *methiodide*, decomp. 200°, yellow powder, whilst *benzyltetrahydroberberine methiodide*, colourless, rhombic plates, has decomp. 224°. Both methiodides, by treatment with silver oxide and 50% alcohol and then with boiling potassium hydroxide, yield the same tertiary base, *de-benzyl-N-methyltetrahydroberberine*, $C_{28}H_{29}O_4N$, m. p. 121—122·5°, colourless, quadratic plates (*sulphate*, m. p. 209—210° ; *hydrochloride*, decomp. 238—240° ; *hydriodide*, m. p. 193—194°). Since de-benzyl-*N*-methyltetrahydroberberine is converted into hydrastinine and 3 : 4-dimethoxy-2-styrylbenzaldehyde by oxidation with sodium dichromate in boiling acetic acid (this fissive oxidation is quite similar
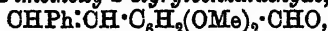
to that of landanosine described by Pyman [T., 1909, **95**, 1267]), it receives the formula :

$$CHPh{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}CH_2{\cdot}CH{<}^{C_6H_2(:CH_2O_2)}_{NMe{-}{-}{-}CH_2}{>}CH_2,$$
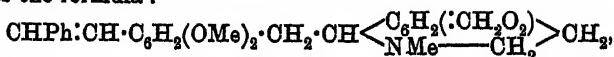
although, perhaps, a constitution containing the annexed skeleton is in better agreement with the facts that the de-base cannot be reduced and does not react with bromine.

3 : 4-*Dimethoxy-2-styrylbenzaldehyde,*

$$CHPh{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}CHO,$$
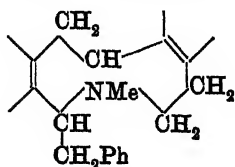
m. p. 71—74°, long, colourless needles, does not react with bromine in chloroform (steric hindrance ?), and forms an *oxime*, m. p. 125—140°, *phenylhydrazone,* m. p. 120—122°, yellow needles, *semicarbazone,* m. p. 190—192°, and *anil,* m. p. 107—109°; by reduction with sodium and warm alcohol, it is converted into 3 : 4-*dimethoxy-2-β-phenylethylbenzyl alcohol,* $CH_2Ph{\cdot}CH_2{\cdot}C_6H_2(OMe)_2{\cdot}CH_2{\cdot}OH$, m. p. 96—98°, colourless needles.

De-benzyl-*N*-methyltetrahydroberberine forms with methyl iodide at 100° a *methiodide,* m. p. 210°, yellow plates, which is converted, by successive treatment with silver oxide and 50% alcohol and with boiling potassium hydroxide, into *de-benzyl-NN-dimethyltetrahydroberberine,* $C_{20}H_{31}O_4N$, m. p. 93—94·5° (*sulphate,* m. p. 197°; *hydrochloride,* m. p. 238°), which cannot be reduced and is given the formula

$$CHPh{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}CH{:}CH{\cdot}C_6H_2(:CH_2O_2){\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2,$$

because it yields 3 : 4-dimethoxy-2-styrylbenzaldehyde by fissive oxidation. It forms a *methiodide,* m. p. 268°, which is decomposed and yields trimethylamine and 3 : 4-*dimethoxy-3' : 4'-methylenedioxy-2-styryl-6'-vinylstilbene,*

$$CHPh{:}CH{\cdot}C_6H_2(OMe)_2{\cdot}CH{:}CH{\cdot}C_6H_2(CH{:}CH_2){<}^{O}_{O}{>}CH_2,$$
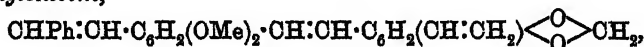
m. p. 120—122°, colourless needles, by the usual treatment.

Benzyldihydroberberine and methyl iodide at 100° yield a *substance,* decomp. 181°, which is not a methiodide, because it loses hydrogen iodide by treatment with alcoholic ammonia and yields a *substance,* $C_{26}H_{27}O_4N$, m. p. 187—188°, pale yellow, rhombic plates, which is called *de-benzyl-N-methyldihydroberberine*; the hydriodide of the latter is identical with the original additive compound. The constitution of de-benzyl-*N*-methyldihydroberberine has not been definitely settled; either of the annexed formulæ may be possible, and serves to explain many of the following transformations of the substance, but objections can be raised against both :
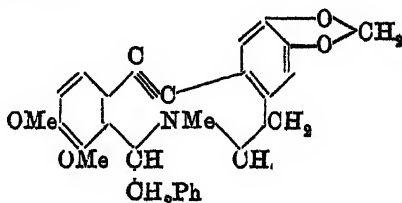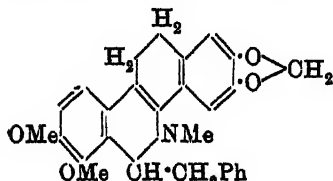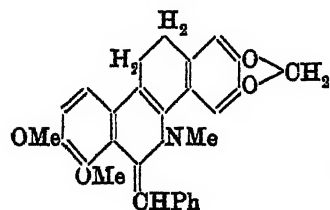
De-benzyl-N-methyldihydroberberine forms a *methiodide*,

$$C_{28}H_{27}O_4NMeI,H_2O,$$
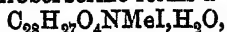
decomp. 167°, reddish-yellow prisms, and is reduced by stannous chloride and boiling alcohol and hydrochloric acid, D 1·19, to the stannichloride of a *substance*, $C_{28}H_{29(or\ 31)}O_4N$, m. p. 162·5—164°, colourless leaflets (*hydrochloride*, decomp. about 215°; *sulphate*, decomp. above 170°), which is called *α-hydro-de-benzyl-*N-*methyldihydroberberine*. It is unchanged by bromine, iodine, or methyl iodide, and has only faintly basic properties. By reduction at a lead cathode in alcohol and 30% sulphuric acid at 40—50°, and with a cathodic current density of 0·075 ampere per sq. cm. and at 24 volts, de-benzyl-N-methyldihydroberberine is converted into a mixture of α-hydro-de-benzyl-N-methyldihydroberberine and a *substance*, $C_{28}H_{29(or\ 31)}O_4N$, m. p. 134—136°, microscopic plates, which is called *β-hydro-de-benzyl-*N-*methyldihydroberberine*. The mixture is readily separated, since only the β-compound forms a *methiodide*. Analysis fails to determine whether the α- and β-compounds are isomeric or whether one contains more hydrogen than the other. The preceding methiodide is converted, by treatment with silver oxide and subsequent boiling with an alkali, into *β-hydro-de-benzyl-*NN-*dimethyldihydroberberine*, $C_{29}H_{31(or\ 33)}O_4N$, m. p. 126°, colourless needles, the *methiodide*, decomp. 239°, of which yields trimethylamine and a non-nitrogenous substance by the usual treatment.

The oxidation of de-benzyl-N-methyldihydroberberine by sodium dichromate and acetic acid at 90° produces, after dilution with water, a yellow (unexamined) solid and a green solution. Sodium carbonate precipitates from the latter *dehydro-de-benzyl-*N-*methyldihydroberberine* (annexed formula), m. p. 203—204°, yellow prisms, which forms a *hydrochloride* and *sulphate*, decomp. 229°, but not a methiodide. By reduction with stannous chloride, alcohol, and concentrated hydrochloric acid, or at a lead cathode in alcohol and 30% sulphuric acid at 40—50°, dehydro-de-benzyl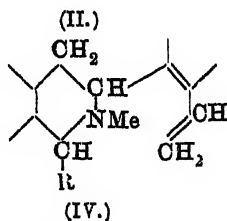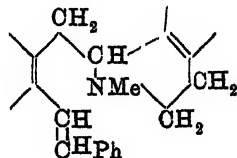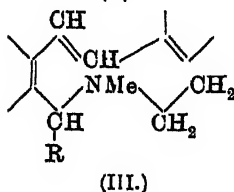-N-methyldihydroberberine is converted into a *substance*, $C_{28}H_{27(or\ 29)}O_4N$, m. p. 164—165°, pale yellow, hexagonal plates, which appears to be isomeric with α-hydro-de-benzyl-N-methyldihydroberberine.

Benzyltetrahydroberberine methiodide in aqueous alcoholic suspension is converted by silver chloride into the *methochloride*, decomp. 228°, rhombic plates, an aqueous solution of which on the water-bath is converted by 5% sodium amalgam into de-benzyl-N-methyltetrahydroberberine and iso*hydro-de-benzyl-*N-*methyltetrahydroberberine*, $C_{28}H_{31}O_4N$, m. p. 96—98°, colourless plates (*hydriodide*, m. p. 229° [decomp.]).

C. S.

Methyldihydroberberine and its Derivatives. MARTIN FREUND and HANNS COMMESSMANN (*Annalen*, 1913, 397, 52—56).—Alkyl- or aryl-dihydroberberines react with methyl iodide to form the hydriodides of bases called de-alkyl-(or aryl-)-N-methyldihydroberberines; by the

electrolytic method, each of the de-bases yields two reduction products, a- and β-hydro-de-alkyl-(or aryl-)-N-methyldihydroberberines. Since these reduction products have similar properties, whether the alkyl or aryl group is methyl, ethyl, *isopropyl*, *isobutyl*, *isoamyl*, benzyl, or phenyl, the de-bases all have the same constitution, namely, that already given for the benzyl compound (Freund and Fleischer, preceding abstract).

By reduction, R-dihydroberberines each yield two stereoisomeric R-tetrahydroberberines, from which two stereoisomeric R-tetrahydroberberine methiodides (formula I) are obtained. (R-Tetrahydroberberines do not combine additively with iodides other than methyl iodide.) By treatment with silver oxide and subsequently with boiling alkali, the two methiodides yield one and the same de-base, which may have the constitution II, III, or IV. When R is CH_2Ph, the de-base has formula II (Freund and Fleischer, preceding abstract); when R is $Pr\beta$, the de-base has constitution III (Freund and Lachmann, following abstract); when R is Me, Et, $CH_2Pr\beta$, $CH_2 \cdot CH_2Pr\beta$, n-C_8H_{17}, or Ph, the de-base has formula IV.

(I.) (II.) (III.) (IV.)
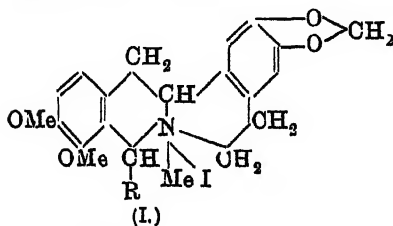
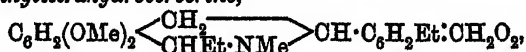*Methyltetrahydroberberine methiodide*, $C_{22}H_{26}O_4NI$, m. p. 263—264°, colourless prisms, is converted by the usual method into *de-methyl-N-methyltetrahydroberberine*, $C_6H_2(OMe)_2 < \begin{array}{l} CH_2 \!-\! CH \!-\! C_6H_2 \!:\! CH_2O_2 \\ CHMe \cdot NMe \quad CH \!:\! CH_2 \end{array}$, m. p. 115—116°, colourless prisms (*hydrochloride*, m. p. 224—225° [decomp.]; *sulphate*, m. p 211—212°; *nitrate*, m. p. 198—199° [decomp.]). The de-base does not yield hydrastinine by oxidation (de-benzyl-N-methyltetrahydroberberine is the only one that does), and forms a *methiodide*, m. p. 257° (decomp.), colourless needles.

Methyldihydroberberine and methyl iodide form the *hydriodide*, m. p. 218° (decomp.), yellowish-green needles, of *de-methyl-N-methyl-dihydroberberine*, $C_{21}H_{23}O_4N$, m. p. 155°, yellow, irregular prisms (*sulphate*, m. p. 116° [decomp.]; *hydrochloride*, m. p. 104°). By electrolytic reduction at a lead cathode in alcohol and 20% sulphuric acid, the de-base is converted into *a-hydro-de-methyl-N-methyldihydroberberine*,

$C_{22}H_{25}O_4N$, m. p. 146° (*sulphate*, m. p. 223° [decomp.]; *hydrochloride*, m. p. 155° [decomp.]; *nitrate*, decomp. 198°), and *β-hydro-de-methyl-N-methyldihydroberberine*, $C_{22}H_{25}O_4N$, m. p. 215° (*sulphate*, m. p. 135—138° [decomp.]; *hydrochloride*, decomp. 220°; *nitrate*, decomp. 234°). The constitutions of the de-base and its reduction products are analogous to those of de-benzyl-*N*-methyldihydroberberine and its reduction products (Freund and Fleischer, preceding abstract). C. S.

Ethyldihydroberberine and Its Derivatives. MARTIN FREUND and HANNS COMMESSMANN (*Annalen*, 1913, **397**, 57—69).—The reduction of ethyldihydroberberine at a lead cathode yields Freund and Mayer's ethyltetrahydroberberine, m. p. 151° (A., 1905, i, 657), and *ψ-ethyltetrahydroberberine*, $C_{22}H_{25}O_4N$, m.p. 117—119°, faintly yellowish-green, irregular plates, which forms a *sulphate*, m. p. 236° (decomp.), *hydrochloride*, decomp. 248°, and *nitrate*, decomp. 210°.

Ethyltetrahydroberberine and methyl iodide at 100° yield the *methiodide*, $C_{22}H_{25}O_4N$MeI, m. p. 228—229°, colourless needles, which is converted by the usual process into *de-N-methyl-a-ethyltetrahydroberberine*,

$$C_6H_2(OMe)_2{<}^{CH_2-CH-C_6H_2 \cdot CH_2O_2}_{CHEt \cdot NMe\ CH:CH_2}$$

m. p. 134° (*hydrochloride*, decomp. 220°; *sulphate*, decomp. 239°; *nitrate*, decomp. 152°). The de-base does not yield hydrastinine by oxidation, is also produced by the successive action of silver oxide and potassium hydroxide on *ψ-ethyltetrahydroberberine methiodide*, m. p. 211° (decomp), and is reduced at a lead cathode in alcohol and 20% sulphuric acid to *hydro-de-N-methylethyltetrahydroberberine*,

$$C_6H_2(OMe)_2{<}^{CH_2}_{CHEt \cdot NMe}{>}CH \cdot C_6H_2Et:CH_2O_2,$$

m. p. 124—125° (*sulphate*, m. p. 230°; *hydrochloride*, m. p. 243°). De-*N*-methylethyltetrahydroberberine and methyl iodide at 100° form the *methiodide*, $C_{23}H_{27}O_4N$MeI, decomp. 230°, which is converted by silver oxide and potassium hydroxide in the usual manner into *de-NN-dimethylethyltetrahydroberberine*, $C_{24}H_{29}O_4N$, m. p. 85—86°. The *methiodide*, m. p. 208—209°, of the latter is decomposed into trimethylamine and 3:4-*dimethoxy*-3':4'-*methylenedioxy*-2-*propenyl*-6'-*vinyl-stilbene*, $CHMe:CH \cdot C_6H_2(OMe)_2 \cdot CH:CH \cdot C_6H_2(:CH_2O_2) \cdot CH:CH_2$, m. p. 82—83°, stout needles, by the usual treatment.
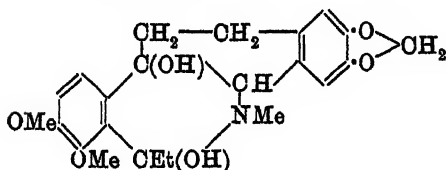
Ethyldihydroberberine and methyl iodide yield the *hydriodide*, m. p. 210° (decomp.), of *de-N-methylethyldihydroberberine*, $C_{23}H_{25}O_4N$, m. p. 142—143°, softening at 136—137°. The de-base forms a *methiodide*, $C_{23}H_{25}O_4N$MeI, m. p. 250° (decomp.), which yields by the usual method of decomposition *de-NN-dimethylethyldihydroberberine*, $C_{24}H_{27}O_4N$, m. p. 115—116° (*sulphate*, m. p. 191—192° [decomp.]; *nitrate*, decomp. 168°; *hydrochloride*, decomp. 163—164°).

The reduction of de-*N*-methylethyldihydroberberine at a lead cathode in alcohol and 20% sulphuric acid yields a mixture of *a-hydro-de-N-methylethyldihydroberberine*, $C_{23}H_{27}O_4N$, m. p. 137°, and *β-hydro-de-N-methylethyldihydroberberine*, $C_{23}H_{27}O_4N$, m. p. 168°. The *a*-base forms a *sulphate*, decomp. 188°, *hydrochloride*, decomp. 266°, and *nitrate*, decomp. 170°, does not form a methiodide, and is converted

into de-*N*-methylethyldihydroberberine by bromine in chloroform and basification of the product. The β-base is unattacked by bromine, and forms a *sulphate*, decomp. 107—108°, *hydrochloride*, decomp. 250°, *nitrate*, decomp. 185°, and *methiodide*, m. p. 245° (decomp.). The decomposition of the last in the usual manner by silver oxide and potassium hydroxide yields a *substance*, m. p. 104—120°, which is probably a mixture of two isomeric β-*hydro-de-*NN-*dimethylethyldihydroberberines* (formulæ I and II); the *methiodide* has decomp. 230°.
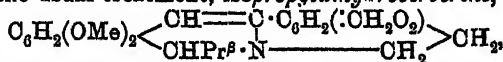

(I.)   (II.)
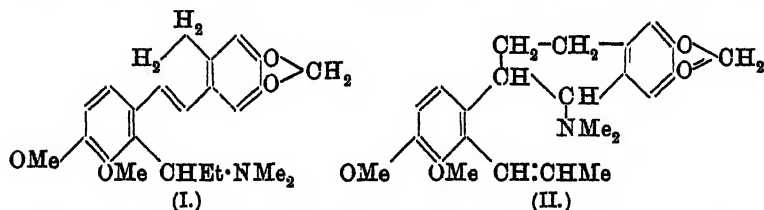
By oxidation with sodium dichromate and acetic acid at 80°, de-*N*-methylethyldihydroberberine yields a *substance*, $C_{28}H_{27}O_6N$, m. p. 130° (decomp.) (*hydr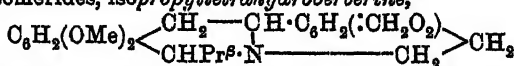ochloride*, m. p. 225°, colourless needles), which is called *oxy-de-N-methylethyldihydroberberine hydrate*, and possibly has the annexed constitution. This substance is also produced by

the oxidation of α- or β-hydro-de-*N*-methylethyldihydroberberine; in addition, a second *substance*, $C_{23}H_{25(or\ 23)}O_4N$, m. p. 178°, yellow crystals, is formed, which is provisionally named iso-*de-N-methylethyldihydroberberine*.   C. S.

*iso*Propyldihydroberberine and its Derivatives. MARTIN FREUND and ROBERT LACHMANN (*Annalen*, 1913, **397**, 70—84).— Berberine sulphate and ethereal magnesium *iso*propyl bromide react to form, after the usual treatment, iso*propyldihydroberberine*,

$$C_6H_2(OMe)_2 \begin{matrix} CH=\!\!=\!C \cdot C_6H_2(:CH_2O_2) \\ CHPr^\beta \cdot N \underline{\hspace{2em}} CH_2 \end{matrix} CH_2,$$

m. p. 167—168°, citron-yellow needles. By electrolytic reduction in alcohol and 20% sulphuric acid at 50—60° and a current density 0·06 ampere per sq. cm. at the cathode, *iso*propyldihydroberberine yields the two stereoisomerides, iso*propyltetrahydroberberine*,

$$C_6H_2(OMe)_2 \begin{matrix} CH_2\underline{\hspace{1em}}CH \cdot C_6H_2(:CH_2O_2) \\ CHPr^\beta \cdot N \underline{\hspace{2em}} CH_2 \end{matrix} CH_2$$

m. p. 157—158°, greenish-yellow, rhombic leaflets (*sulphate*, m. p. 197° [decomp.]; *nitrate*, decomp. 215°; *hydrochloride*, decomp. 226°; *platinichloride*, decomp. 205°; *perchlorate*, m. p. 226—227° [decomp.]), and ψ-iso*propyltetrahydroberberine*, m. p. 200—202°, colourless prisms (*nitrate*, decomp. 176°; *hydrochloride*, decomp. 254°). By treatment with alcoholic iodine at 100°, *iso*propyltetrahydroberberine is converted

into iso*propyldihydroberberine* *hydriodide*, $C_{23}H_{25}O_4N,HI,Et\cdot OH$, decomp. 110°, brown, rhombic plates, whilst the ψ-base is simply converted into its hydriodide.

iso*Propyltetrahydroberberine* *methiodide*, m. p. 210° (decomp.), colourless needles, and ψ-iso*propyltetrahydroberberine* *methiodide*, decomp. 247—248°, faintly yellow needles, each yield, by treatment with silver oxide and 50% alcohol, and subsequently with boiling potassium hydroxide, a mixture of a-*de-N-methyl*iso*propyltetrahydroberberine*, $C_{24}H_{29}O_4N$, m. p. 132·5° (*sulphate*. decomp. about 200°; *hydriodide*, decomp. 197°, yellow needles), and b-*de-N-methyl*iso*propyltetrahydroberberine*, $C_{24}H_{29}O_4N$, m. p. 102—103° (*hydrochloride*, decomp. 226°; *hydriodide*, decomp. 218°; *nitrate*, decomp. 197°). The a-*de*-base is converted into the b-*de*-base by boiling alcohol, and yields ψ-iso*propyltetrahydroberberine* methiodide by digestion with aqueous alcohol and subsequent treatment with acetic acid and potassium iodide; it is unchanged by boiling nitrobenzene, by boiling dilute sulphuric acid and alcohol, or by electrolytic reduction. The b-*de*-base is comparatively stable. By prolonged boiling with glacial acetic acid and subsequent treatment of the basified and filtered solution with potassium iodide, it yields a *methiodide*, m. p. 236°, from which the b-*de*-base is regenerated directly.

Of all the *de*-bases examined by the authors (preceding and following abstracts), a-*de-N*-methyl*iso*propyltetrahydroberberine is the only one which resembles Gadamer and Voss's ethyl anhydro-base of tetrahydroberberine (A., 1910, i, 415) in being readily re-converted into the ammonium base or its salts by digestion with water or acids. The a-*de*-base, therefore, is given the constitution

$$C_6H_2(OMe)_2 \begin{array}{c} CH:CH\cdot C_6H_2(:CH_2O_2) \\ CHPr^\beta\cdot NMe\text{———}CH_2 \end{array} > CH_2,$$
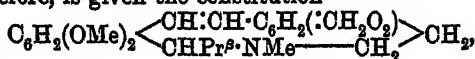
analogous to that of the ethyl anhydro-base of tetrahydroberberine. The b-*de*-base and all other de-alkyl (or -aryl-)-*N*-methyltetrahydroberberines have the only remaining constitution:

$$C_6H_2(OMe)_2 \begin{array}{c} CH_2\text{—}CH\text{—}C_6H_2:CH_2O_2 \\ CHR\cdot NMe \quad CH:CH_2 \end{array}$$
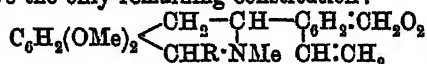
(compare preceding abstract). Given these constitutions, the preceding transformations of a- and b-*de-N*-methyl*iso*propyltetrahydroberberine become readily explicable. By electrolytic reduction, the b-*de*-base yields *hydro-b-de-N-methyl*iso*propyltetrahydroberberine*,
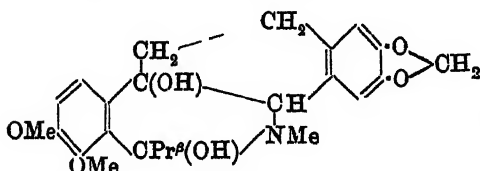
$$C_6H_2(OMe)_2 \begin{array}{c} CH_2\text{———}CH\cdot C_6H_2Et:CH_2O_2 \\ CHPr^\beta\cdot NMe \end{array}$$
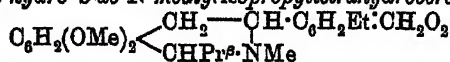
colourless needles containing alcohol, m. p. 74—80° (*hydrochloride*, $C_{24}H_{31}O_4N,HCl$, decomp. 261°).

b-*De-N-methyl*iso*propyltetrahydroberberine methiodide*, $C_{24}H_{29}O_4NMeI$, colourless prisms (the a-*de*-base does not form a methiodide), is converted by the usual method into *de-NN-dimethyl*iso*propyltetrahydroberberine*, $C_{25}H_{31}O_4N$, m. p. 112—115°, colourless needles (*sulphate*, decomp. about 190°). iso*Propyldihydroberberine* and methyl iodide at 100° yield the *hydriodide*, decomp. 229°, yellow needles, of *de-N-methyl*iso*propyldihydroberberine*, $C_{24}H_{27}O_4N$ (for constitution, compare Freund and Fleischer, preceding abstract), m. p. 170—171°, pale

yellow crystals (*perchlorate*, decomp. 213°; *methiodide*, decomp. 232°, golden-yellow, rhombic prisms).

The electrolytic reduction of de-N-methyl*iso*propyldihydroberberine in alcohol and 20% sulphuric acid at 50—60° yields a mixture of a - *hydro* - *de* - N - *methyliso*propyldihydroberberine, $C_{24}H_{29}O_4N$, m. p. 164·5—166°, greenish-yellow, rhombic plates (*nitrate*, decomp. 185°, rhombic plates; *sulphate*, m. p. 197°, prisms; *hydrochloride*, m. p. about 218°, needles; *hydriodide*, m. p. 234°; *perchlorate*, decomp. 236°), and β - *hydro* - *de* - N - *methyliso*propyldihydroberberine, $C_{24}H_{29}O_4N$, m. p. 184—186°, almost colourless, rhombic prisms (*nitrate*, decomp. 188°; *hydriodide*, decomp. 226—227°). The a-compound does not form a methiodide, and yields de-N-methyl*iso*propyldihydroberberine by treatment with bromine in chloroform and basification of the product. The β-base forms a *methiodide*, $C_{24}H_{29}O_4N,MeI$, decomp. 253°, and is unchanged by bromine. By oxidation with sodium dichromate and acetic acid at 80—90°, de-N methyl*iso*propyldihydroberberine and its a- and β-hydro-derivatives each yield the same product, *hydroxy-de-*N-*methyl*isopropyldi*hydroberberine hydroxide* (annexed formula?), decomp. 129°, light brown crystals, which forms a *hydrochloride*, decomp. about 205°, and *hydriodide*, decomp. 238°. C. S

*iso*Butyldihydroberberine and Its Derivatives. MARTIN FREUND and HAROLD HAMMEL (*Annalen*, 1913, 397, 85—93).—iso-*Butyldihydroberberine*, $C_{24}H_{27}O_4N$, m. p. 112—113°, yellow needles, leaflets, or prisms, prepared in the usual manner from berberine hydrochloride and ethereal magnesium *iso*butyl bromide, forms a *nitrate*, m. p. 205° (decomp.), pale yellow leaflets, *hydriodide*, m. p. 223° (decomp.), yellow leaflets, and *platinichloride*, decomp. 220°, orange needles. It reacts with methyl iodide to form the *hydriodide*, m. p. 206° (decomp.), pale yellow needles, of *de-*N-*methyl*isobutyldihydro*berberine*, $C_{25}H_{29}O_4N$, m. p. 147—148° (*hydrochloride*, m. p. 148° [decomp.]; *platinichloride*, m. p. 217°; *hydrobromide*, m. p. 115—120° [decomp.]). The de-base is unchanged by bromine in chloroform, and forms a *methiodide*, $C_{25}H_{29}O_4NMeI$, m. p. 172° (decomp.), pale yellow leaflets, which is converted in the usual manner into *de-*NN-*dimethyl-isobutyldihydroberberine*, $C_{26}H_{31}O_4N$, m. p. 130—131°, almost colourless plates. The *methiodide* of the last substance, $C_{26}H_{31}O_4NMeI$, m. p. 164° (decomp.), yellow needles, decomposes into methyl iodide and the original base when heated at about 95° or boiled with aqueous alcoholic potassium hydroxide; the base is also obtained when the methiodide is treated successively with silver oxide and boiling potassium hydroxide.

By reduction at a lead cathode in alcohol and 25% sulphuric acid, de-N-methyl*iso*butyldihydroberberine yields a mixture of a-*hydro-de-*N-*methylisobutyldihydroberberine*, $C_{25}H_{31}O_4N$, m. p. 158—160°, almost

colourless, rhombic plates (*hydrobromide*, decomp. 223°; *hydriodide*, m. p. 189°), and β-*hydro-de-*N-*methyl*iso*butyldihydroberberine*, $C_{25}H_{31}O_4N$, m. p. 179° (*hydrochloride*, decomp. about 240°; *hydrobromide*, m. p. 239°; *hydriodide*, m. p. 239° [decomp.]). The α-compound does not form a methiodide, and is converted into de-N-methyliso*butyldi*-hydroberberine by treatment with bromine in chloroform and basification of the product. The β-compound is unchanged by bromine, and forms a *methiodide*, $C_{25}H_{31}O_4N,MeI$, m. p. 246° (decomp.), which regenerates the β-compound by heating at 240°, and is converted by successive treatment with silver oxide and boiling potassium hydroxide into β-*hydro-de-*NN-*dimethyl*iso*butyldihydroberberine*, $C_{26}H_{33}O_4N$, m. p. 136—137°, colourless, rhombic leaflets. By electrolytic reduction at a lead cathode in sulphuric acid, isobutyldihydroberberine yields a mixture of iso*butyltetrahydroberberine*, $C_{24}H_{29}O_4N$, m. p. 127—129°, greenish-yellow, rhombic leaflets (*hydrochloride*, m. p. 237°; *hydriodide*, m. p. 256°; *sulphate*, m. p. 234°; *methiodide*, m. p. 193°), and ψ-iso*butyl-tetrahydroberberine*, $C_{24}H_{29}O_4N$, m. p. 197°, colourless plates (*hydro-chloride*, m. p. 270—273° [decomp.]; *hydriodide*, m. p. 250° [decomp.]).

C. S.

n-Octyldihydroberberine and isoAmyldihydroberberine and their Derivatives. MARTIN FREUND and DANIEL STEINBERGER (*Annalen*, 1913, **397**, 94—106).—A suspension of berberine sulphate in ether, by treatment with ethereal magnesium *n*-octyl iodide and decomposition of the product by ice and hydrochloric acid, yields the *hydriodide*, $C_{28}H_{35}O_4N,HI,H_2O$, m. p. 122—124°, reddish-brown crystals, of *octyl-dihydroberberine*, $C_{28}H_{35}O_4N$, m. p. 88·5—89°, yellow needles. In a similar manner, berberine sulphate and magnesium iso*amyl bromide, after the addition finally of concentrated potassium iodide, yield the *hydriodide*, decomp. 141°, yellow crystals, of iso*amyldihydroberberine*, $C_{25}H_{29}O_4N$, an amorphous, yellow substance.

By reduction with stannous chloride, hydrochloric acid, D 1·19, and alcohol, isoamyldihydroberberine yields only iso*amyltetrahydroberberine*, $C_{25}H_{31}O_4N$, m. p. 95—96° (*sulphate*, decomp. 237°; *hydriodide*, decomp. 255°; *nitrate*, decomp. 209—210), whilst by reduction at a lead cathode in alcohol and 20% sulphuric acid at 40—50°, it yields, in addition, ψ-iso*amyltetrahydroberberine*, $C_{25}H_{31}O_4N$, m. p. 172° (*hydrochloride*, decomp. 231—232°; *hydriodide*, decomp. 239—240°; *nitrate*, decomp. 210—211°).

iso*Amyltetrahydroberberine methiodide*, decomp. 191°, and ψ-iso*amyl-tetrahydroberberine methiodide*, decomp. 223—224°, each yield, by the usual method of decomposition, de-N-*methyl*iso*amyltetrahydroberberine*, which forms a *hydrochloride*, $C_{25}H_{33}O_4N,HCl$, decomp. 185°, *sulphate*, decomp. 190—191°, and *hydriodide*, decomp. 224—225°, and does not yield hydrastinine by oxidation.

iso*Amyldihydroberberine and methyl iodide at 100° yield the *hydriodide* of de-N-*methyl*iso*amyldihydroberberine*, $C_{26}H_{31}O_4N$, m. p. 102°, pale yellow plates. By reduction with stannous chloride, hydro-chloric acid, and alcohol, the de-base yields α-*hydro-de-*N-*methyl*iso-*amyldihydroberberine*, $C_{26}H_{33}O_4N$, m. p. 128°, rhombic leaflets, which forms a *sulphate*, decomp. 187—188°, *nitrate*, decomp. 146°, *hydro-*

chloride, decomp. 232°, and *hydriodide,* decomp. 228°, does not form a methiodide, and is converted into de-*N*-methyl*iso*amyldihydroberberine by treatment with bromine in chloroform. By reduction at a lead cathode, de-*N*-methyl*iso*amyldihydroberberine yields, in addition to the preceding α-compound, *β-hydro-de-*N*-methyl*isoamyldihydroberberine,* $C_{26}H_{31}O_4N$, m. p. 145°, rhombic prisms (*hydrochloride,* decomp. 220—221°; *hydriodide,* decomp. 226—227°; *methiodide,* m. p. 260°).

By prolonged heating with alcoholic ammonia in the presence of air, *iso*amyldihydroberberine hydriodide is converted into *dehydroisoamyl-dihydroberberine,*

$$C_6H_2(OMe)_2 \big\langle {}^{C \!=\!\!=\!\!=\! C \cdot C_6H_2(:CH_2O_2)}_{C(C_5H_{11}) \cdot N \text{———} CH_2} \big\rangle CH_2(?),$$
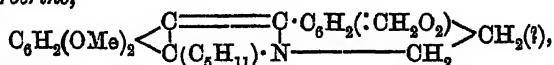
m. p. 249° (decomp.), hexagonal, yellow plates, which rapidly darken in the air and light. The dehydro-compound yields *iso*amyl- and ψ-*iso*-amyl-tetrahydroberberines by electrolytic reduction, does not form salts with acids in the cold, and by boiling for eight to ten minutes with 96% alcohol and 20% hydrochloric acid or sulphuric acid, D 1·215, is converted into the *hydrochloride,* $C_{25}H_{29}O_5N,HCl$, decomp. 204°, yellow needles, or the *sulphate,* $C_{25}H_{29}O_5N,H_2SO_4$, decomp. 265°, yellow needles, of *hydroxyisoamyldihydroberberine,*

$$C_6H_2(OMe)_2 \big\langle {}^{C(OH) \!=\!\!=\!\! C \cdot C_6H_2(:CH_2O_2)}_{CH(C_5H_{11}) \cdot N \text{———} CH_2} \big\rangle CH_2,$$
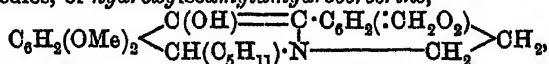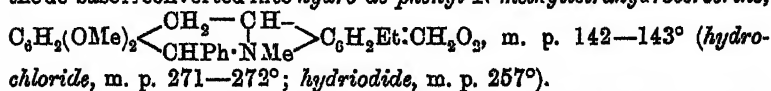
m. p. 120—125°, sintering at 65°, dark yellow needles; a by-product of both reactions is a *substance,* decomp. 180—185°, reddish-brown, rhombic crystals.　　　　　　　　　　　　　　　　　　　　　　　　　　　C. S.

Phenyldihydroberberine and its Derivatives. MARTIN FREUND aud EUGEN ZORN (*Annalen,* 1913, **397,** 107—117).—Phenyldihydro-berberine (Freund and Beck, A., 1905, i, 151) forms a *hydrochloride,* m. p. 160°, yellow prisms, *sulphate,* decomp. 170°; pale yellow needles, *nitrate,* decomp. 224°, and *hydriodide,* m. p. 215°. By reduction at a lead cathode in alcohol and 30% sulphuric acid, it yields Gadamer's phenyltetrahydroberberine (*sulphate,* decomp. 241°), and ψ-*phenyltetra-hydroberberine,* $C_{26}H_{25}O_4N$, m. p. 204—205°, white needles (*hydriodide,* m. p 235°); only the former can be isolated when the reduction is effected by stannous chloride and boiling alcohol and hydrochloric acid.

Phenyltetrahydroberberine methiodide, m. p. 243°, faintly yellow plates, and ψ-*phenyltetrahydroberberine methiodide,* m. p. 247°, white crystals, yield methyl iodide and the respective bases by heating. By treatment with silver oxide and boiling potassium hydroxide in the usual manner, each methiodide yields *de-phenyl-*N*-methyltetrahydroberberine,*

$$C_6H_2(OMe)_2 \big\langle {}^{CH_2 \text{—} CH \text{—} C_6H_2:CH_2O_2}_{CHPh \cdot NMe \quad CH:CH_2} ,$$
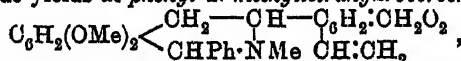
m. p. 153°, which forms a *hydrochloride,* m. p. 232°, *hydriodide,* decomp. 208°, and *methiodide,* m.p. 238° (decomp.). By reduction at a lead cathode, the de-base is converted into *hydro-de-phenyl-*N*-methyltetrahydroberberine,*

$$C_6H_2(OMe)_2 \big\langle {}^{CH_2 \text{—} CH-}_{CHPh \cdot NMe} \big\rangle C_6H_2Et:CH_2O_2,\text{ m. p. 142—143° (}hydro\text{-}$$

chloride, m. p. 271—272°; *hydriodide,* m. p. 257°).

Phenyltetrahydroberberine methiodide is converted into the metho-

chloride in dilute alcohol, and the latter, after evaporation of the alcohol, is treated with 5% sodium amalgam on the water-bath. The product is 2-mp-*dimethoxy*-o-*benzylbenzylhydrastinine*,

$$CH_2Ph\cdot C_6H_2(OMe)_2\cdot CH_2\cdot CH{<}{\overset{\textstyle C_6H_2(:CH_2O_2)}{\underset{\textstyle NMe\text{——}CH_2}{}}}{>}CH_2,$$
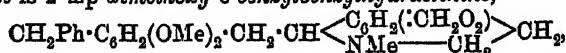
m. p. 109·5—110·5°, colourless plates (*hydriodide*, m. p. 217—219°), from which hydrastinine is obtained by oxidation with sodium dichromate and acetic acid at 90°.

Phenyldihydroberberine and methyl iodide at 100° yield the *hydriodide*, m. p. 245°, yellow prisms, of *de-phenyl-N-methyldihydroberberine*, $C_{27}H_{25}O_4N$, m. p. 178—179°, yellow prisms (*sulphate*, m. p. 160°; *methiodide*, decomp. 220°). By reduction at a lead cathode in cold alcohol and 30% sulphuric acid, the de-base is converted into a mixture of *a-hydro-de-phenyl-N-methyldihydroberberine*, $C_{27}H_{27}O_4N$, m. p. 178—179°, yellow, rhombic prisms (*sulphate*, m. p. 206°, colourless prisms; no methiodide), and *β-hydro-de-phenyl-N-methyldihydroberberine*, $C_{27}H_{27}O_4N$, m. p. 211—212°, rhombic plates (*hydrochloride*, m. p. 257°; *methiodide*, m. p. 247—248°, pale yellow leaflets).   C. S.

Preparation of Morphine Esters of Halogenated Fatty Acids. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 256156. Compare this vol., i, 385).—*Dichloroacetylmorphine*, a yellow powder, decomp. 204°, is obtained when cooled anhydrous morphine (5 parts) is slowly treated with chloroacetyl chloride (10 parts) and subsequently heated at 90—100°.

Chloroacetylmorphine, colourless crystals, decomp. 227°, is obtained by the partial hydrolysis of the preceding compound or by employing 6 parts of chloroacetyl chloride in the foregoing preparation. *Di-a-bromoisovalerylmorphine*, sintering at 61° and decomposing at 133°, is formed by the action of a-bromoisovaleryl chloride on morphine in the presence of pyridine.   F. M. G. M.

The Symmetry of Sparteine. LOUIS CORRIEZ (*Chem. Zentr.*, 1913, i, 29; from *Bull. Sci. Pharmacol.*, 1912, 19, 602—610. Compare Moureu and Valeur, A., 1912, i, 296).—An attempt to prove the symmetry of the sparteine molecule was made by decomposing the hydrochloride of a-sparteine methochloride and the hydrobromide of a-sparteine methobromide in a vacuum at 250°, but the reaction was of a complicated nature, since the resulting sparteine haloids partly decomposed into sparteine. An attempt to obtain the same iodobromide by treating sparteine iodide with hydrogen bromide and sparteine bromide with hydrogen iodide was also without success. A homogeneous, faintly yellow *iodobromide*, $C_{15}H_{26}N_2,HI,HBr,H_2O$, was obtained in the former case, in cubes with $[a]_D - 16°21'$, but the latter process led to a mixture, containing, in all probability, the dibromide, di-iodide, and iodobromide.   J. C. W.

Hæmopyrrole. OSKAR PILOTY and JOSEF STOCK (*Ber.*, 1913, 46, 1008—1013. Compare A., 1912, i, 923).—Crude hæmopyrrole has been separated into two fractions, the one, hæmopyrrole-I, consisting of a mixture of bases which give crystalline salts with picric acid in ethereal solution; the other, hæmopyrrole-II, comprising bases which

either do not form a picrate or of which the picrates are soluble in ether. The hæmopyrrole-II fraction comprises only 12—13% of the whole; it consists as to more than one-half of pyrroles with less than eight atoms of carbon, the remainder containing pyrroles with eight carbon atoms. It consists of at least three components differing from the five hæmopyrroles already known, and the lowest boiling fraction forms a very soluble, orange-coloured picrate, m. p. 108°, whilst a high boiling fraction closely resembles bis-dimethyl-pyrrole (Piloty and Wilke, A., 1912, i, 899). E. F. A.

Preparation of a Dichloroisatin [and of 5 : 7-Dichloroisatin]. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 255772 and 255774. Compare A., 1909, i, 966).—When an aqueous solution or suspension of isatin, or of 5-chloroisatin (m. p. 247°), is chlorinated at the ordinary temperature in the presence of potassium iodide, it gives rise to an unstable *dichloroisatin*, which crystallises from acetic acid in hard, red crystals, and has m. p. 155°; when this is dissolved in sodium hydrogen sulphite it loses chlorine, and the subsequent addition of acid precipitates 5-chloroisatin, whilst by the action of concentrated sulphuric acid at 80° in the presence of iodine the labile chlorine atom migrates into the ring, yielding 5 : 7-dichloroisatin (m. p. 221°).
F. M. G. M.

Preparation of a Dichlorobromoisatin. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 255773 and 255775. Compare preceding abstract).—When an aqueous suspension of 5-bromoisatin is treated at about 15° with chlorine in the presence of potassium iodide, it furnishes a *chloro-5-bromoisatin* (red prisms, m. p. 145°), in which the chlorine atom is labile and eliminated by the action of sodium hydrogen sulphite, whilst with concentrated sulphuric acid at 80° in the presence of potassium iodide it yields 7-*chloro-5-bromoisatin*, yellow needles, m. p. 231°. F. M. G. M.

Lepidylamine. PAUL RABE (*Ber.*, 1913, 46, 1024—1025).— 4-Cyanoquinoline is reduced, either on treatment with nascent hydrogen or on shaking with molecular hydrogen and a palladium sol, to 4-*aminomethylquinoline* (*lepidylamine*), $C_6H_4 < ^{C(CH_2 \cdot NH_2)}_{N ===CH} > CH$. This is a colourless oil, b. p. 172°/8 mm., but becomes violet on exposure to the air. The *monohydrochloride*, which is neutral to litmus, forms a colourless, crystalline powder, m. p. 206—208° (decomp.), which becomes blue on exposure to air. The *dihydrochloride* crystallises in well formed, colourless needles, decomp. above 250°. It is acid to litmus. E. F. A.

Quinolyl Ketones. I. PAUL RABE and RICHARD PASTERNACK (*Ber.*, 1913, 46, 1026—1032).—By the interaction of magnesium phenyl bromide and ethyl cinchonate under special conditions, phenyl 4-quinolyl ketone, m. p. 60°, is obtained. This differs from the compound, m. p. 294°, described under the same name by Remfry and Decker (A., 1908, i, 364). In addition to ketones the esters of quinoline-4-

carboxylic acid give rise to carbinols when submitted to the Grignard synthesis. Similarly, 4-cyanoquinolines give rise to ketones and amines ; thus 4-cyanoquinoline and magnesium ethyliodide yield 4-quinolyl ethyl ketone and 4-quinolyldiethylaminomethane. In addition some quantity of 4-ethylquinoline is formed.

4-Benzylquinoline is a viscid, strongly refractive, yellow oil, b. p. 222—223°/19 mm. ; the *sulphate* forms colourless, rhombic crystals + $2H_2O$, m. p. 105—108°, or anhydrous, m. p. 132—133°. The *picrate* forms yellow prisms and plates, m. p. 178° ; the *methiodide* crystallises in orange plates, m. p. 226°.

Phenyl 4-quinolyl ketone, m. p. 60°, yields the following salts : the picrate, crystallising in pale yellow, interlaced needles, m. p. 220° ; a *picrolonate*, forming dark yellow, rhombic crystals, decomp. 174° ; an orange *methiodide*, with metallic lustre, m. p. 218° ; an *oxime hydrochloride*, separating in matted needles, m. p. 256° (decomp.).

4-Quinolylethylketone is a yellow oil, b. p. 163—166°/8—9 mm. ; the *acetate* forms colourless needles, m. p. 87°. The *oximino*-derivative crystallises in short, colourless crystals, decomp. about 220°.

4-Quinolyldiethylcarbinol crystallises in lustrous, colourless plates, m. p. 135°, b. p. 192—198°/13 mm.

4-Quinolyldiethylaminomethane crystallises in colourless plates, m. p. 126°.   E. F. A.

Quinolyl Ketones. II. PAUL RABE and RICHARD PASTERNACK (*Ber.*, 1913, **46**, 1032—1034).—Ethyl quinolinecarboxylates in presence of sodium ethoxide condense with esters of the general constitution $R_1 \cdot CH_2 \cdot CO_2 R_2$; thus ethylcinchonate and ethylacetate combine to form *ethyl-γ-quinoloylacetate*, $\begin{matrix} N \cdot C_6 H_4 \\ CH \cdot CH \end{matrix} > C \cdot CO \cdot CH_2 \cdot CO_2$, a yellow oil, which could not be distilled unchanged, and is characterised by forming a sparingly soluble acid sulphate. When heated with 25% sulphuric acid, 4-quinolyl methyl ketone is obtained.

Similarly, ethyl quinate and ethyl propionate condense to form *ethyl β-[6-methoxy-4-quinoloyl]-propionate*. This is characterised by the *picrate* crystallising in slender, yellow needles, m. p. 137—138°, and the *picrolonate*, orange, matted needles, decomp. 136°.
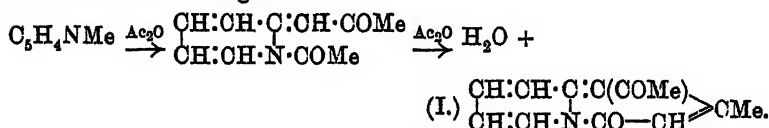
β-6-Methoxyquinolyl ethyl ketone, obtained on hydrolysis, crystallises in pale yellow needles, m. p. 57—58°.   E. F. A.

Nature of Picolide and Pyrindole. Action of Propionic Acid on α-Picoline. MAX SCHOLTZ and W. FRAUDE (*Ber.*, 1913, **46**, 1069—1082. Compare A., 1912, i, 385, 648).—Derivatives of pyrrocoline have previously been prepared by Angeli (A., 1890, 1156), who termed the compound pyrindole, and this name is now adopted by the authors.
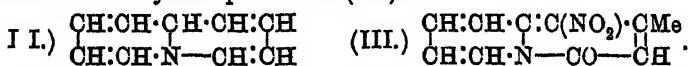
From the absence of basic properties and the formation of condensation products with only one molecule of phenylhydrazine, hydroxylamine, and semicarbazide, the conclusion is drawn that picolide contains one of its carbonyl groups directly attached to the nitrogen atom. This view is confirmed by the fact that towards alkyl

magnesium haloids, picolide behaves as a monoketone; it reacts with nly one molecule of the organo-magnesium compound, yielding tertiary alcohols of the formula $C_{10}H_8ON \cdot CMeR \cdot OH$.
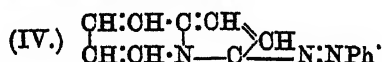
The reactions of picolide and its transformation into pyrindole are best represented by the formula I, its formation from a-picoline being shown in the following scheme :

$$C_5H_4NMe \xrightarrow{Ac_2O} \begin{array}{l} CH{:}CH \cdot C{:}CH \cdot COMe \\ CH{:}CH \cdot N \cdot COMe \end{array} \xrightarrow{Ac_2O} H_2O +$$

$$(I.) \begin{array}{l} CH{:}CH \cdot C{:}C(COMe) \\ CH{:}CH \cdot N \cdot CO \text{---} CH \end{array}{>}CMe.$$

On account of its relationship to quinoline, the parent ring system (II) is termed quinolizine. Picolide is thus acetylmethylketoquinolizine, whilst the mono-nitro-compound obtained by the action of nitric acid is nitromethylketoquinolizine (III) :

$$(I\,I.) \begin{array}{l} CH{:}CH \cdot CH \cdot CH{:}CH \\ CH{:}CH \cdot N \text{---} CH{:}CH \end{array} \qquad (III.) \begin{array}{l} CH{:}CH \cdot C{:}C(NO_2) \cdot CMe \\ CH{:}CH \cdot N \text{---} CO \text{---} CH \end{array}.$$

Pyrindole couples with diazonium salts in acid solution, yielding crystalline azo-compounds, and reacts with acetic anhydride and benzoyl chloride to form an acetyl and benzoyl derivative. The position of the azo- and acyl-groups has not been definitely established, but from the analogous reactions with pyrrole it is assumed that the groups enter the a-position to the pyrrole ring; benzene-azopyrindole thus receives the formula :

$$(IV.) \begin{array}{l} CH{:}CH \cdot C{:}CH \\ CH{:}CH \cdot N \text{---} C \end{array}{>}\!{<}^{CH}_{} N{:}NPh.$$

A number of other reactions, illustrating the similarity in the behaviour of pyrindole on the one hand and pyrrole and indole derivatives on the other, are also described.

The ready formation of picolide from a-picoline and acetic anhydride has induced the authors to investigate the behaviour of a-picoline towards other anhydrides, but only in the case of propionic anhydride could a definite product be isolated. The reaction proceeds in a manner entirely different to that occurring when acetic anhydride is employed, the resulting compound being a 2-pyridyl-3-ethyl-Δ^3-*cyclo*pentenone :

$$(V.)\ CH{<}^{CH{:}CH}_{CH \text{---} N}{>}C \cdot CH{<}^{CO \text{---} CH_2}_{OEt{:}CH}.$$
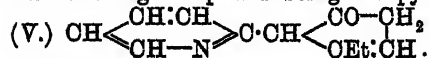
The following condensation products were obtained by condensing aromatic aldehydes with picolide by means of sodium hydroxide in alcoholic solution :

Di-o-nitrobenzylidenepicolide, yellowish-brown crystals, which begin to decompose at 200°, m. p. 220°; the isomeric *meta-* and *para-* compounds have m. p. 212° and 316° respectively; *mono-p-nitrobenzylidenepicolide*, orange needles, m. p. 242°; *tetramethyldi-p-aminobenzylidenepicolide*, from *p*-dimethylaminobenzaldehyde, forms orange needles, m. p. 227°; *dianisylidenepicolide*, m. p. 212°.

Picolide reacts with magnesium methyl iodide to form the *compound,* $C_{10}H_8NO \cdot CMe_2 \cdot OH$, crystallising in long, yellow needles, m. p. 169°,

and with magnesium phenyl bromide, yielding the *compound*,

$$C_{10}H_8ON \cdot CMePh \cdot OH,$$
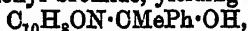
which forms colourless, felted needles, m. p. 178°.

Benzeneazopyrindole (formula IV) crystallises in red needles, m. p. 109°, and *pyrindoleazo-p-toluene* in reddish-brown needles, m. p. 98°.

α-*Naphthaleneazopyrindole* forms a brown, crystalline powder, which begins to melt at 120° and then decomposes.

Benzoylpyrindole, $C_8H_6N \cdot COPh$, prepared by the interaction of pyrindole and benzoyl chloride at the ordinary temperature, crystallises in yellow needles, m. p. 96°.

Pyrindole reacts with carbonyl chloride in toluene solution to form *pyrindolecarboxyl chloride*, $C_8H_6N \cdot COCl$, which crystallises in colourless needles, m. p. 81°, and is hydrolysed by aqueous sodium hydroxide to *pyrindolecarboxylic acid*, needles, m. p. 135° (decomp.).
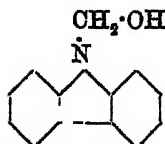
Diquinonylpyrindole,
$$\begin{array}{c} CH{:}CH \cdot C{=\!=\!=}C \cdot C_6H_4O_2 \\ CH{:}CH \cdot N \cdot CH{:}C \cdot C_6H_4O_2 \end{array},$$
prepared from pyrindole and quinone in alcoholic solution, forms deep blue crystals, m. p. above 350°, and resembles the diquinonyldimethylpyrrole described by Möhlau and Redlich (A., 1912, i, 129°).

Pyrindole condenses with ethyl acetoacetate in alcoholic solution in the presence of hydrochloric acid, yielding *ethyl dipyrindoleacetoacetate*,
$$\begin{array}{c} CH{:}CH \cdot C{=\!=\!=}C \cdot CMe(CH_2 \cdot CO_2Et) \cdot C{=\!=\!=}C \cdot CH{:}CH \\ CH{:}CH \cdot N \cdot CH{:}C \cdot OMe(CH_2 \cdot CO_2Et) \cdot C{:}CH \cdot N \cdot CH{:}CH \end{array},$$
crystallising in microscopic, yellowish-green needles, m. p. 140°.

2-*Pyridyl*-3-*ethyl*-Δ³-*cyclopentenone* (V), prepared by heating α-picoline and propionic anhydride at 220°, forms colourless needles, m. p. 86°, and yields a *semicarbazone*, yellow needles, m. p. 201°.   F. B.

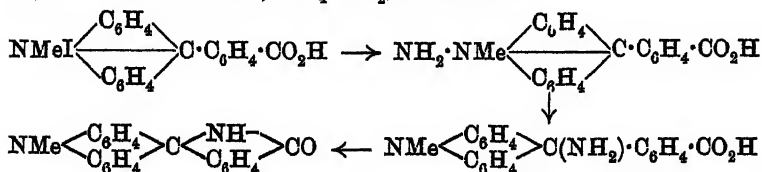**Preparation of Methylolcarbazole.** MARTIN LANGE (D.R.-P. 256757).—*Methylolcarbazole* (annexed formula) is obtained when a boiling alcoholic solution of carbazole (16·7 parts) is treated with anhydrous potassium carbonate (10 parts) and a 40% solution of formaldehyde (10 parts); on cooling, the product separates; it forms colourless needles, m. p. 127—128°, with an evolution of formaldehyde; mineral acids convert it into methylenecarbazole.   F. M. G. M.

Preparation of N-Alkylcarbazolesulphonic Acids. LEOPOLD CASSELLA & Co. (D.R.-P. 256718. Compare A., 1910, i, 775).— Sulphonated N-alkylcarbazoles have not been prepared, although di- and tri-sulphonyl derivatives of carbazole itself are known. *Ethyl carbazolesulphonic acid* is obtained when fused N-ethylcarbazole (195 parts) is slowly treated with forty parts of concentrated sulphuric acid, heated at 120° and subsequently at 150—160°, and the mixture finally treated with sodium carbonate; the *barium*, *calcium*, *sodium*, and *potassium* salts are crystalline powders.

When fused with an alkali hydroxide, these compounds furnish hydroxy-N-alkylcarbazoles, which condense with p-nitrosophenols to yield indophenolsulphonic acids.   F. M. G. M.
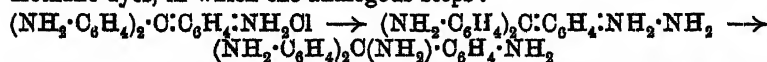
Ammonium-amides and the Action of Amines on Cyclammonium Salts and Analogous Compounds. HERMAN DECKER and PAUL BECKER (*Ber.*, 1913, **46**, 969—978).—It has already been shown that the action of ammonia or amines on the quaternary salts of phenylacridinecarboxylic acid yields not only the lactone, but also the lactam of aminophenylmethyldihydroacridinecarboxylic acid (Decker and Schenk, A., 1906, i, 304), and it was suggested that the change takes place with the intermediate formation of a compound corresponding to ammonium-amide, $NH_4 \cdot NH_2$, the scheme :

$$NMeI \underset{C_6H_4}{\overset{C_6H_4}{<}} C \cdot C_6H_4 \cdot CO_2H \rightarrow NH_2 \cdot NMe \underset{C_6H_4}{\overset{C_6H_4}{<}} C \cdot C_6H_4 \cdot CO_2H$$

$$NMe \underset{C_6H_4}{\overset{C_6H_4}{<}} C \underset{C_6H_4}{\overset{NH-}{<}} CO \leftarrow NMe \underset{C_6H_4}{\overset{C_6H_4}{<}} C(NH_2) \cdot C_6H_4 \cdot CO_2H$$

representing the probable series of changes. This view was confirmed by several considerations, and it is now greatly strengthened by the discovery that the parent substance, phenylacridine methiodide, is converted by concentrated ammonia into 5-amino-5-phenyl-10-methyldihydroacridine, $NMe \underset{C_6H_4}{\overset{C_6H_4}{<}} CPh \cdot NH_2$. This finally disposes of any idea that the previous product may have been due to the action of ammonia on the previously formed lactone. The cause of the rearrangement is supposed to be the tendency of the positive amino-group to migrate from the positive nitrogen atom to a negative carbon atom. That such a substance as $NH_2 \cdot NMe \underset{C_6H_4}{\overset{C_6H_4}{<}} CPh$, which is assumed as the first product of the above reaction, should be capable of at least a fleeting existence is indicated by the formation of carbinylamines by the action of ammonia on the salts of the triphenylmethane dyes, in which the analogous steps :

$$(NH_2 \cdot C_6H_4)_2 \cdot C \colon C_6H_4 \colon NH_2Cl \rightarrow (NH_2 \cdot C_6H_4)_2 C \colon C_6H_4 \colon NH_2 \cdot NH_2 \rightarrow$$
$$(NH_2 \cdot C_6H_4)_2 C(NH_2) \cdot C_6H_4 \cdot NH_2$$

probably occur (Noelting and Saas, this vol., i, 522; Villiger and Kopetschni, A., 1912, i, 1030). The structurally related xanthylium and thioxanthylium salts also yield carbinylamines with ammonia. The possibility, that the acridinium salts may be of the carbonium structure which has been suggested for the triphenylmethane colours is very slight, as the former eliminate methyl iodide exceedingly readily, even, for example, when exposed in aqueous solution to daylight for several weeks.

5-Amino-5-phenyl-10-methyldihydroacridine, small, colourless rods, m. p. 121—122°, is obtained by the gradual addition of a concentrated solution of phenylacridine methiodide to a large excess of 20% ammonia solution ; if a dilute solution of ammonia in slight excess is allowed to act on the methiodide, the product is hydroxyphenylmethyldihydroacridine, which is ver similar in appearance, and this accounts for the divergence of the results of Decker, Hock, and Djiwonsky (A., 1902,

i, 830) and of Hantzsch (A., 1902, i, 113, 126). The above amino-compound dissolves in dilute acids, undergoing scission into phenyl-methylacridinium and ammonium salts; when heated with alcohol, with or without the addition of a little sodium hydroxide, ammonia is again obtained, together with the 5-ethoxy-5-phenyl-10-methyldihydro-acridine, colourless prisms, m. p. 112—113°, which is also obtained by similar treatment of the hydroxyphenylmethyldihydroacridine itself. When warmed with aniline, both the above amino-compound (a carbinylamine) and the corresponding hydroxy-compound are converted into the *carbinylanilide* with elimination of a molecule of ammonia and of water respectively.

If a solution of a phenylxanthylium salt is introduced into ammonia solution a mixture of the amino-compound and of the carbinol is obtained (compare Bunzly and Decker, A., 1904, i, 912); for the preparation of the pure amino compound the phenylxanthylium ferri-chloride, m. p. 169°, was introduced as a fine powder into 20% ammonia solution under benzene; the resultant carbinylamine (9-*amino*-9-*phenyl-xanthen*), $O<^{C_6H_4}_{C_6H_4}>CPh\cdot NH_2$, leaflets, m. p. 112—113°, is extracted by the benzene; when boiled with alcohol it is converted into the ethyl ether of phenylxanthenol (Bünzly and Decker, *loc. cit.*). The formation of the carbinylamine is believed to follow the same course as with the corresponding acridine compound.

9-*Amino*-9-*phenylthioxanthen*, yellowish-red prisms, m. p. 118—120°, is obtained in a similar manner by the action of ammonia on phenyl-thioxanthylium ferrichloride, and undergoes similar conversion into the ethyl ether of thioxanthenol.

The recent discovery of Zincke and Weisspfennig (this vol., i, 389) of dinitrodiphenylamine amongst the reaction products of aniline and 2-dinitrophenyl*iso*quinolinium chloride is held to be a further confirma-tion of the existence of the ammonium-amides and of their decomposi-tion according to the equation: $NA_4\cdot NR_2 = NA_3 + NR_2A$, where A represents an alkyl radicle.   D. F. T.

Preparation of Anthracene Derivatives Containing Nitrogen.
FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 256297. Compare A., 1908, i, 456, 699; 1909, i, 263).—α-*Chloropyridanthrone*, yellowish-white needles, m. p. 260°, is prepared by the action of phosphorus pentachloride on the previously described 2-hydroxy-pyridanthrone (I); it reacts readily with primary aromatic amines to furnish compounds of the general formula (II).

(I.)   (II.)
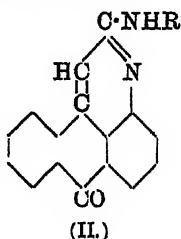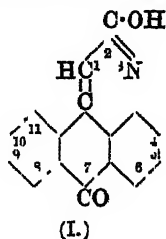
2(1')-*Anthraquinonylaminopyridanthrone* is thus obtained by condensation with 1-aminoanthraquinone in nitrobenzene solution in the presence of copper iodide and sodium acetate ; it does not melt below 300°. The analogous *compound* from aniline has m. p. 227—229°.

<div align="right">F. M. G. M.</div>

Syntheses in the Group of the Indogenides. ANDRÉ WAHL and P. BAGARD (*Compt. rend.*, 1913, **156**, 898—901).—An endeavour to prepare, by the condensation of substituted isatins with oxindole, a new series of indogenides of the type $X<^{C_6H_3R}_{CO}>C:C<^{C_6H_3R'}_{CO}>Y$, where X and Y may be identical or different bivalent atoms or groups, and R and R' any substituents. These condensations did not, however, go so simply as in the case of isatin itself and oxindole (compare A., 1909, i, 330). Thioisatin and oxindole yields not thio-3 . 3'-bisindole, as expected, but "thioindigo scarlet," $NH<^{C_6H_4}_{CO}>C:C<^{CO}_{S}>C_6H_4$ (compare Kalle, D R -P. 241327). 1-Methylisatin on the other hand behaves like isatin itself, and gives 1-*methyl*iso*indigotin*,

$$NH<^{C_6H_4}_{CO}>C:C<^{C_6H_4}_{CO}>NMe,$$
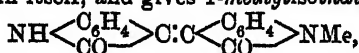
brown needles.

2-Methylisatin when mixed with oxindole in acetic acid solution containing a little aqueous hydrochloric acid is hydrolysed and the product of condensation is simply 3 : 3'-bisindole. If the action takes place in an anhydrous medium in the cold, indirubin is formed. This thus furnishes an easy and rapid method of preparing indirubin, and gives a 90% yield.

<div align="right">W. G.</div>

[**Preparation of 1-Chloronitro-2 : 4-diacetylphenylenediamine.**] AKTIEN-GESELLSCHAFT FUR ANILINFABRIKATION (D.R.-P. 255858).—1-Chloro-2 : 4-phenylenediamine gives rise to a diacetyl derivative which on nitration furnishes 1-*chloronitro* 2 : 4-*diacetylphenylenediamine*, m. p. 234—235°, and on hydrolysis yields 1-*chloronitro*-2 : 4-*phenylenediamine*, m. p. 170°.

<div align="right">F. M. G. M.</div>

Existence of Phenyldi-imide. WILHELM VAUBEL (*Ber.*, 1913, **46**, 1115—1116. Compare A , 1900, i, 522) —An acknowledgment of the criticism of Forster and Withers (T., 1913, **103**, 266) as to the nature of the compound described as phenyldi-imide.

<div align="right">H. W.</div>

[**Preparation of Anthraquinone Derivatives**] FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 256626).—3-*Bromo-4-amino-anthraquinoneacridone*, a blue powder, m. p. 260—270°, is obtained when 3-bromo-4-amino-1-anthraquinonylanthranilic acid is heated at 30° with chlorosulphonic acid.

<div align="right">F. M. G. M.</div>

[**Preparation of Indigoid Compounds.**] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 255691. Compare A., 1906, i, 696).—The *compound*, $C_6H_4<^{NH}_{CO}>C:C<^{CH}_{C_6H_4}>N$, dark red needles, m. p. 212°

<div align="right">*n n* 2</div>

(decomp.), is obtained by the action of alkali hydroxides on indoxyl; if the action is allowed to proceed further, it gives rise to the *compound*, $C_6H_4\text{<}^{NH-}_{CO_2H}\text{>}CH:C\text{<}^{CH}_{C_6H_4}\text{>}N$, and this, when boiled with an alkali carbonate, furnishes anthranilic acid and β-indolealdehyde (*loc. cit.*).   F. M. G. M.

Action of Aliphatic Ketones on Indole and its Homologues : Polymeric Indoles. MAX SCHOLTZ (*Ber.*, 1913, **46**, 1082—1089).— Indole and its 2-methyl derivative condense with acetone, yielding compounds of the type: (I) $N\text{<}^{C_6H_4}_{CH}\text{>}C\text{<}^{CMe_2}_{CMe_2}\text{>}C\text{<}^{C_6H_4}_{CH}\text{>}N$ and

(II) $NH\text{<}^{C_6H_4}_{CH}\text{>}C\cdot CMe_2\cdot C\text{<}^{C_6H_4}_{CH}\text{>}NH$, accordingly as the condensation is effected by means of hydrochloric acid or acetic acid. Similar products are obtained from methyl ethyl ketone, but not from diethyl ketone.

Bisdimethyl-2-methylindolidenemethane,

$$C_8H_4NMe\text{<}^{CMe_2}_{CMe_2}\text{>}C_8H_4NMe,$$
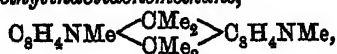
obtained in the form of its *hydrochloride* (colourless needles, m. p. 172°) by the addition of hydrochloric acid to an alcoholic solution of 2-methylindole and acetone, crystallises in colourless needles, m. p. 183°; the *hydrobromide*, prepared in a similar manner, has m. p. 172°.

Bis-2-methylindyldimethylmethane, $CMe_2(C_8H_5NMe)_2$, is obtained by boiling 2-methylindole with glacial acetic acid; it crystallises in colourless leaflets, m. p. 197°.

Bismethylethyl-2-methylindolidenemethane,

$$C_8H_4NMe\text{<}^{CMeEt}_{CMeEt}\text{>}C_8H_4NMe,$$
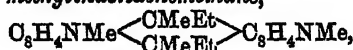
prepared from methyl ethyl ketone, using hydrochloric acid as the condensing agent, forms colourless leaflets, m. p. 97°; the *hydrochloride* crystallises in colourless needles, m. p. 166°.

Ethyl acetoacetate and 2-methylindole yield *ethyl 2-methylindolideneacetoacetate*, $N\text{<}^{C_6H_4}_{CMe}\text{>}C:CMe\cdot CH_2\cdot CO_2Et$, crystallising in long, colourless needles, m. p. 124°.

Bisdimethylindolidenemethane (formula I), prepared from indole and acetone, forms light yellow needles, m. p. 170°; the *hydrochloride* crystallises in orange-yellow needles, m. p. 169°.

Bisindyldimethylmethane (II) forms colourless prisms, m. p. 165°.

An alcoholic solution of indole, on treatment with hydrochloric acid at the ordinary temperature, yields the *hydrochloride* of tri-indole, crystallising in prisms, m. p. 183°; replacement of the hydrochloric acid by hydrobromic acid gives rise to the *hydrobromide* of di-indole, which forms slender, colourless needles (compare Keller, this vol., i, 403).   F. B.

The Constitution of the Pyrazolinecarboxylic Acids. III. AUGUST DARAPSKY (*Ber.*, 1913, **46**, 863—867).—An experimental

investigation in favour of the view that the condensation products of the esters of the diazo-aliphatic acids with the esters of unsaturated carboxylic acids are in reality pyrazoline derivatives and not azine compounds with open-chain structure (compare Darapsky, this vol., i, 297; A., 1912, i, 391; Bülow, this vol., i, 101; A., 1912, i, 134, 316).

The reduction of 4-phenylpyrazole-3 : 5-dicarboxylic acid by sodium amalgam and water at 80—90° gave the same 4-phenylpyrazolidine-3 : 5-dicarboxylic acid (Buchner and Perkel, A., 1904, i, 101) as was obtained by a similar reduction of 4-phenylpyrazoline-3 : 5-dicarboxylic acid. The temperature of decomposition of the product ranges between 220° and 226° according to the rate of heating. D. F. T.

Constitution of Hypnal. DEMETRIUS E. TSAKALOTOS (*Bull. Soc. chim.*, 1913, [iv], 13, 281—285).—Béhal and Choay (A., 1893, i, 301) have obtained two substances by the action of chloral on antipyrine, to which they assign the formulæ below, the first of which is used in

$$
\begin{array}{ll}
\text{CH—CO} & \text{CH—CO} \\
\| \quad \text{>NPh} & \| \quad \text{>NPh(OH)·CH(OH)·CCl}_3 \\
\text{CMe·NMe(OH)·CH(OH)·CCl}_3 & \text{CMe·NMe(OH)·CH(OH)·CCl}_3 \\
\quad \text{(I.)} & \quad \text{(II.)}
\end{array}
$$
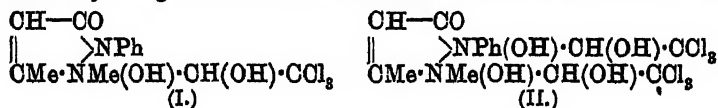
pharmacy under the name hypnal. For the second, the author proposes the name bihypnal. The substances have m. p. 62·3° and 61·8° respectively, whereas Béhal and Choay found 67—68° for either substance.

The author has examined the freezing-point curve of mixtures of chloral hydrate and antipyrine, and finds that it rises to a maximum at the two points at which chloral hydrate : antipyrine = 2 : 1 and = 1 : 1 respectively. From the general form of the curve, he is led to the conclusion that hypnal and bihypnal are molecular compounds, which, he considers, explains the practical identity of their m. p.'s

H. W.

Some New Derivatives of Piperazine. MARIO GHIGLIENO (*Atti R. Accad. Sci. Torino*, 1912–13, 48, 534—538).—When cyanacetic ester and anhydrous piperazine are heated together for one hour at 100—115°, *biscyanoacetylpiperazine*, $C_4H_8N_2(CO·CH_2·CN)_2$, is formed; it crystallises in colourless or slightly yellow needles, m. p. 248—250° (decomp.). When ordinary hydrated piperazine is used in the reaction, the corresponding *amide*, $C_4H_8N_2(CO·CH_2·CO·NH_2)_2$, is obtained; it crystallises in colourless needles or in prisms, which decompose about 174—175° when rapidly heated. The substance is acid in reaction, and gives metallic salts. It is converted into the dicarboxylic acid only with great difficulty. Anhydrous piperazine, m. p. 104°, is obtained by keeping ordinary piperazine over calcium chloride for a long time. R. V. S.

Pyrimidines. LX. Alkylation with Benzyl Chloride. TREAT B. JOHNSON and ZAI ZIANG ZEE (*Amer. Chem. J.*, 1913, 49, 287—294). —Johnson and Derby (A., 1908, i, 1018) studied the action of benzyl chloride in presence of sodium ethoxide on certain derivatives

of 2-ethylthiol-6-pyrimidone, and found that in all cases the corresponding *N*-benzyl compounds were produced. It was shown that the substitution of a methyl group in the 4- or 5-position and a bromine atom or ethoxy-group in the 5-position of the ring does not favour the formation of 6-benzoxypyrimidines. The present work was undertaken with the object of investigating the action of benzyl chloride on a 2-thiol-6-pyrimidone in which both the 4- and 5-positions are substituted, and of determining whether a strongly negative group in the 4-position would favour the production of an *O*-benzyl derivative.

Ethyl 2-amino-5-methyl-6-pyrimidone-4-carboxylate,

$$NH<\begin{array}{c}C(NH_2){:}N\\CO{-}CMe\end{array}>C{\cdot}CO_2Et,$$
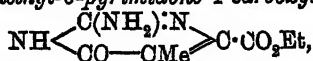
obtained in small yield by the action of the sodium salt of ethyl oxalylpropionate on guanidine thiocyanate in presence of sodium hydroxide, forms prismatic needles, and does not show a definite m. p.

Ethyl 2-ethylthiol-1-benzyl-5-methyl-6-pyrimidone-4-carboxylate,

$$CH_2Ph{\cdot}N<\begin{array}{c}C(SEt){:}N\\CO{-}CMe\end{array}>C{\cdot}CO_2Et,$$
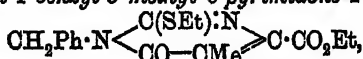
m. p. 69—71°, prepared by heating ethyl 2-ethylthiol-5-methyl-6-pyrimidone-5-carboxylate with benzyl chloride in presence of sodium ethoxide, crystallises in colourless needles, and when hydrolysed with concentrated hydrochloric acid is converted into 1-*benzyl-5-methyl-pyrimid-2 : 6-dione-4-carboxylic acid,*

$$CH_2Ph{\cdot}N<\begin{array}{c}CO{-}NH\\CO{\cdot}CMe\end{array}>C{\cdot}CO_2H,$$

m. p. 277—279° (decomp.), which forms hexagonal tablets. When the latter compound is heated at 285—295° until effervescence ceases, 1-*benzyl-5-methylpyrimid-2 : 6-dione* (1-*benzylthymine*),

$$CH_2Ph{\cdot}N<\begin{array}{c}CO{-}NH\\CO{\cdot}CMe\end{array}>CH,$$
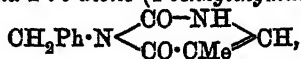
m. p. 203—205°, is obtained, which forms prismatic crystals.

An attempt was made to alkylate ethyl 5-methylpyrimid-2 : 6-dione-4-carboxylate with benzyl chloride in presence of sodium ethoxide, but without success.   E. G.

[Phenazine] Correction. FRIEDRICH KEHRMANN (*Ber.*. 1913, **46**, 1220. Compare this vol., i, 298).—Fischer and Hepp (A., 1897, i, 257) had already observed that rosindones resulted by the action of alkalis on alkylnaphthaphenazonium salts. The author still holds that the green methylphenazonium iodide is a quinhydrone salt (compare Hantzsch, this vol., i, 393.)   J. C. W.

The Triphenylmethane Colour Bases. EMILIO NOELTING and J. SAAS (*Ber.*, 1913, **46**, 952—967).—The authors have convinced themselves that the action of ammonia on triphenylmethane dyes is, as was believed by von Baeyer (A., 1910, i, 249), more complex than was at first supposed (Noelting & Philipp, A., 1908, i, 295). An independent investigation of the products of the action of ammonia has been recently published by Villiger and Kopetschni (A., 1912, i, 1030).

Commercial crystal-violet always contains some of the pentamethyl compound, which can be detected by acetylation, dissolving in water, and partly immersing in the liquid a piece of filter paper ; the green colour of the acetyl derivative of the pentamethyl compound rises in the paper more rapidly than the violet. Even when Michler's ketone is condensed with pure dimethylaniline in the presence of phosphoryl chloride, the condensation product contains a quantity of pentamethyl compound. The product contains least pentamethyl compound if a large excess of the amine is taken for the condensation. The colourless substance obtained from the action of ammonia on crystal-violet is the carbinylamine, $NH_2 \cdot C(C_6H_4 \cdot NMe_2)_3$; it separates from a mixture of benzene and ligroin in prismatic tablets, m. p. 193—195°. The action of diethylamine on a solution of crystal-violet, on the other hand, precipitates the carbinol, m. p. 194—195°, which after recrystallisation has m. p. 207—209° (compare Villiger and Kopetschni, *loc. cit.*), whilst trimethylamine solution produces at first a violet solution of the ammonium base, $OH \cdot NMe_2 \cdot C_6H_4(C_6H_4 \cdot NMe_2)_2$, which shortly begins to lose its colour and to deposit the carbinol in a pure state.

Ethyl-violet (hexaethyltriaminotriphenylcarbinol), obtained from tetraethyldiaminobenzophenone, diethylaniline and phosphoryl chloride alone, or mixed with benzene at 100°, on precipitation with potassium hydroxide yielded the free colourless carbinol, $OH \cdot C(C_6H_4 \cdot NEt_2)_3$, m. p. 136—137°. When recrystallised from alcohol, the carbinol undergoes partial etherification, and the *ethyl ether*, $OEt \cdot C(C_6H_4 \cdot NEt_2)_3$, m. p. 127—128°, can be readily obtained by the action of sodium ethoxide. The *carbinylamine*, $NH_2 \cdot C(C_6H_4 \cdot NEt_2)_3$, of ethyl-violet forms colourless needles, m. p. 141·5—142·5°.

Victoria-Blue *B*, obtained by purification of the commercial article and by condensation of pure Michler's ketone with phenyl-α-naphthylamine, forms deep blue tablets, m. p. 247—249°. No corresponding carbinol, carbinyl ether and amine were isolable, as the action of alkalis yielded only an *imine* base, $NPh \cdot C_{10}H_6 \cdot C(C_6H_4 \cdot NMe_2)_2$, deep violet, prismatic tablets, which is hydrolysed by dilute sulphuric acid to Michler's ketone and phenyl-α-naphthylamine (compare Nathanson and Müller, A., 1889, 1188).

Night-Blue, m. p. 219—220°, yields an analogous *imine* base,

$$C_6H_4Me \cdot N \cdot C_{10}H_6 \cdot C(C_6H_4 \cdot NMe_2)_2,$$

deep violet, prismatic tablets, which can also be hydrolysed to its components, Michler's ketone, and tolyl-α-naphthylamine.

α-Naphthol-Blue (tetramethyldiaminonaphthafuchsone), the condensation product of Michler's ketone, and α-naphthol, when pure, forms dark-coloured prisms, m. p. 266—270°; *hydrochloride*, green needles ; *platinichloride*, dark coloured. No carbinol, carbinyl ether, or carbinylamine could be isolated ; it gives a green *acetyl* derivative, and on reduction in acetic acid by zinc dust a *leuco-base*,

$$OH(C_6H_4 \cdot NMe_2)_2 \cdot C_{10}H_6 \cdot OH,$$

prisms, m. p. 187—188°.

Naphtho-Blue (Noelting and Philipp, *loc. cit.*), the condensation product of Michler's ketone and dimethyl-α-naphthylamine, can be separated into a coloured and a colourless constituent ; the latter is, as

earlier suggested, the carbinol, $OH \cdot C(C_6H_4 \cdot NMe_2)_2 \cdot C_{10}H_6 \cdot NMe_2$, but the former is actually identical with α-Naphthol-Blue, and must be produced by a partial elimination of dimethylamine during the neutralisation of the reaction product; the product also always contains some pentamethyl compound, $C(C_6H_4 \cdot NMe_2)_2 \cdot C_6H_4 \cdot NMe,HCe$, due to a loss of a methyl group similar to that observed in the preparation of crystal-violet. For the preparation of the pure colourless carbinol of Naphtho-Blue it is advisable to use in the condensation an excess of dimethyl-α-naphthylamine, and then to render the solution of the product alkaline at as low a temperature as possible. Treatment of the aqueous solution of the chloride with ammonia yields the colourless carbinylamine, m. p. 173—175°.   D. F. T.

5-Aminopyrazole and Iminopyrines. III. 5-Imino-1-phenyl-3-methylpyrazolone. AUGUST MICHAELIS and ARTHUR SCHÄFER (*Annalen.*, 1913, **397**, 119—148. Compare A., 1911, i, 1037; 1905, i, 476).—*1-Phenyl-3-methyl-4 : 5-azipyrazole,* $N{<}^{NPh \cdot C}_{CMe \cdot CH}{>}N$, m. p. 109°, yellowish-brown leaflets, prepared by warming 5-amino-1-phenyl-3-methylpyrazole (5-imino-1-phenyl-3-methylpyrazolone) in 50% acetic acid with concentrated hydrogen peroxide, is converted into 5-amino-1-phenyl-3-methylpyrazole by reducing agents and into 4-halogeno-5-amino-1-phenyl-3-methylpyrazoles by warming with concentrated halogen acids. *4-Chloro-1-phenyl-3-methyl-4 : 5-azipyrazole,* m. p. 103°, red leaflets, is obtained by treating 4-chloro-5-amino-1-phenyl-3-methylpyrazole with hydrogen peroxide as above, or, in hydrochloric acid, with concentrated sodium nitrite. It is also obtained by leading chlorine into a hydrochloric acid solution of 5-amino-1-phenyl-3-methylpyrazole. The last method has enabled the authors to explain the constitution of the trichloro-compound obtained by Michaelis and Brust (*loc. cit.*); this is not 4-chloro-5-amino-1-dichlorophenyl-3-methylpyrazole as stated previously, but *4-chloro-5-dichloroamino-1-phenyl-3-methylpyrazole,* m. p. 60°, since it yields 4-chloro-1-phenyl-3-methyl-4 : 5-azipyrazole by warming with water. Unlike the non-halogenated compound, 4-chloro-1-phenyl-3-methyl-4 : 5-azipyrazole is unchanged by halogen acids; it is reduced to 4-chloro-5-amino-1-phenyl-3-methylpyrazole by boiling concentrated sodium hyposulphite. *4-Bromo-1-phenyl-3-methyl-4 : 5-azipyrazole,* $C_{10}H_8N_3Br$, m. p. 101°, reddish-brown leaflets, prepared by similar methods to the chloro-compound, yields 4-bromo-5-amino-1-phenyl-3-methylpyrazole by reduction, and is converted into *4 : 4-dibromo-5-imino-1-phenyl-3-methylpyrazolone,*

$$NPh{<}^{N=\!=\!=CMe}_{C(:NH) \cdot CBr_2},$$
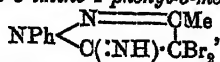
m. p. 126°, colourless needles, and *4-chloro-4-bromo-5-imino-1-phenyl-3-methylpyrazolone,* m. p. 124°, colourless needles, by warming with hydrobromic acid or hydrochloric acid, and subsequently basifying with ammonia. *4-Iodo-1-phenyl-3-methyl-4 : 5-azipyrazole,* $C_{10}H_8N_3I$, m. p. 194°, yellowish-red needles, prepared by the oxidation of 4-iodo-5-amino-1-phenyl-3-methylpyrazole or by heating 5-amino-1-phenyl-3-methylpyrazole with alcoholic iodine and sodium hydroxide at 150°, is

unchanged by halogen acids, and is converted into 4-iodo-5-amino-1-phenyl-3-methylpyrazole by reduction. 1-*Phenyl*-3 : 4-*dimethyl*-4 : 5-*azipyrazole*, $C_{11}H_{11}N_3$, m. p. 105°, red leaflets, is prepared by oxidising 5-amino-1-phenyl-3 : 4-dimethylpyrazole in hydrochloric acid by hydrogen peroxide; it is soluble in concentrated halogen acids and is precipitated unchanged by alkalis. 4 : 5-*Anilo-1-phenyl-3-methylpyrazole*,

$$N\!\!<^{\text{NPh}\cdot\text{C}}_{\text{CMe}\cdot\text{C}}\!\!\!\!>\!\!NPh,$$

m. p. 169°, red leaflets or brownish-red needles, is prepared by treating a glacial acetic acid solution of 4-benzeneazo-5-amino-1-phenyl-3-methylpyrazole with concentrated sodium nitrite, whereby nitrogen and nitric oxide are evolved. By reduction with tin and alcoholic hydrochloric acid, it yields benzene and 4-amino-1-phenyl-3-methyl-5-pyrazolone hydrochloride, by the oxidation of which in the air rubazonic acid is produced. 4-β-*Naphthaleneazo-5-amino-1-phenyl-3-methylpyrazole*, $C_{20}H_{17}N_5$, m. p. 117°, yellow leaflets, prepared from β-naphthalenediazonium chloride and 5-amino-1-phenyl-3-methylpyrazole in aqueous sodium carbonate, is converted in a similar manner into 4 : 5-β-*naphthylimino-1-phenyl 3-methylpyrazole*, $C_{20}H_{15}N_3$, m. p. 178°, reddish-brown needles, by the reduction of which naphthalene and 4-amino-1-phenyl-3-methylpyrazole are formed.

5-*Formylamino-1-phenyl-3-methylpyrazole*, $C_{11}H_{11}ON_3$, m. p. 135°, colourless needles, prepared from the aminopyrazole and formic acid on the water-bath, and the corresponding *benzoylamino*-derivative, $C_{17}H_{15}ON_3$, m. p. 113°, long needles, have been prepared; the latter is converted into 4 *bromo-5-benzoylamino-1-phenyl-3-methylpyrazole*, m. p. 172°, by bromine in dilute acetic acid. 5-*Benzenesulphonylamino-1-phenyl-3-methylpyrazole* has m. p. 170°. 5-Acetylamino-1-phenyl-3-methylpyrazole and benzenediazonium chloride yield a *substance*,

$$C_{39}H_{41}O_4N_7,$$
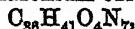
m. p. 107°, yellow needles, which is being investigated.

Hot aqueous potassium cyanate and 5-amino-1-phenyl-3-methyl-pyrazole hydrochloride yield 5-*carbamido-1-phenyl-3-methylpyrazole*,

$$NH_2\cdot CO\cdot NH\cdot C\!\!<^{\text{NPh}\cdot\text{N}}_{\text{CH}-\text{CMe}},$$

m. p. 215°, colourless needles.

5-Amino-1-phenyl-3-methylpyrazole and phenylcarbimide yield, by heating, 5-*phenylcarbamido-1-phenyl-3-methylpyrazole*, m. p. 205°; the *phenylthiocarbamido*-derivative, m. p. 150°, is prepared in a similar manner. The 5-aminopyrazole and carbon disulphide at 150° yield the s-*thiocarbamide*, $CS(NH\cdot C_{10}H_9N_2)_2$, m. p. 184°.

5-Amino-1-phenyl-3-methylpyrazole can be almost completely diazotised in nearly concentrated hydrochloric acid (compare Mohr, A., 1909, i, 190); the solution does not contain 4-oximino-5-imino-1-phenyl-3-methylpyrazolone, and yields coloured precipitates with alkaline β-naphthol and resorcinol. 1-*Phenyl-3-methylpyrazole-5-azoresorcinol*, $C_{16}H_{14}O_2N_4$, yellow needles, has m. p. 250°. 1-Phenyl-3-methyl-pyrazole-5-diazonium chloride and 1-phenyl-3-methyl-5-pyrazolone in acetic acid slowly form 1-*phenyl-3-methylpyrazole-5(4')-azo-1'-phenyl-3'-methyl-5'-pyrazolone*,

$$^{\text{N}-\text{NPh}}_{\text{CMe}\cdot\text{CH}}\!\!>\!\!C\cdot N_2\cdot CH\!\!<^{\text{CO}-\text{NPh}}_{\text{CMe:N}},$$

m. p. 175°, yellowish-red needles, which is soluble in alkalis. 5-*Diazoamino-*

1-*phenyl*-3-*methylpyrazole*, $C_{10}N_2H_9 \cdot N_2 \cdot NH \cdot C_{10}N_2H_9$, m. p. 182°, yellow leaflets, is obtained by treating 5-amino-1-phenyl-3-methylpyrazole in hydrochloric acid with less than 1 mol. of sodium nitrite, or by carefully treating the completely diazotised solution with aqueous sodium hydroxide.

5-Amino-1-phenyl-3-methylpyrazole and benzaldehyde at 135° yield 4-*benzylidenebis*-5-*amino*-1-*phenyl*-3-*methylpyrazole*, $CHPh(C_{10}N_3H_{10})_2$, m. p. 66°, faintly yellow powder, which forms a *hydrochloride*,
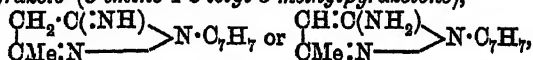
$$C_{27}H_{25}N_6, 2HCl,$$
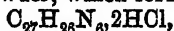
m. p. 218° (*platinichloride*, yellowish-red crystals), in the cold, but is converted into its generators by hot acids. The corresponding *o-nitrobenzylidene*, *salicylidene*, and *anisylidene* compounds, m. p. 89°, 120°, and 219° respectively, are described.   C. S.

5-Amino-1-*o*- and *p*-tolyl-3-methylpyrazoles. August Michaelis and Ludwig Klappert (*Annalen*, 1913, **397**, 149—159) —*Aceto-acetonitrile-o-tolylhydrazone*, $CN \cdot CH_2 \cdot CMe : N \cdot NH \cdot C_7H_7$, m. p. 115°, colourless needles, prepared from acetoacetonitrile and *o*-tolylhydrazine in 30% acetic acid, is converted, by heating with alcoholic hydrochloric acid at 120° for three hours and basifying, into 5-*amino*-1-*o*-*tolyl*-3-*methylpyrazole* (5-*imino*-1-*o*-*tolyl*-3-*methylpyrazolone*),

$$\begin{matrix} CH_2 \cdot C(:NH) \\ CMe:N \end{matrix}\!\!>\!\!N \cdot C_7H_7 \text{ or } \begin{matrix} CH:C(NH_2) \\ CMe:N \end{matrix}\!\!>\!\!N \cdot C_7H_7,$$

m. p. 93°, b. p. 314°, colourless crystals (*hydrochloride*, m. p. 113°), which reacts in hydrochloric acid with chlorine, in glacial acetic acid with bromine, and in alcohol with iodine, to form, after basifying, 4-*chloro*-5-*amino*-1-*o*-*tolyl*-3-*methylpyrazole*, m. p. 114°, and the 4-*bromo*-compound, m. p. 134°, and the 4-*iodo* compound, m. p. 141°, respectively. By prolonged treatment with chlorine, a hydrochloric acid solution of 5-amino-1-*o*-tolyl-3-methylpyrazole yields 4-*chloro*-1-*o*-*tolyl*-3-*methyl*-4 : 5-*azipyrazole*, $N\!\!<\!\!\begin{matrix} CMe\text{---}CCl \\ N(C_7H_7)C \end{matrix}\!\!>\!\!N$, m. p. 107°, red leaflets.   4-*Bromo*-1-*o*-*tolyl*-3-*methyl*-4 : 5-*azipyrazole*, m. p. 115°, red needles, and the 4-*iodo*-compound, m. p. 133°, reddish-brown leaflets, are prepared in a similar manner by means of bromine in acetic acid, and by alcoholic iodine at 140—150°.

5-Amino-1-*o*-tolyl-3-methylpyrazole is converted into 5-*acetylamino*-1-*o*-*tolyl*-3-*methylpyrazole*, m. p. 157°, colourless needles, by boiling acetic anhydride, into 4-*benzeneazo*-5-*amino*-1-*o*-*tolyl*-3-*methylpyrazole*, m. p. 118°, yellow leaflets, by benzenediazonium chloride in hydrochloric acid and subsequent addition of sodium carbonate, into 4-*oximino*-5-*imino*-1-*o*-*tolyl*-3-*methylpyrazolone*, m. p. 195°, red crystals, by sodium nitrite and 30% acetic acid, and into 5-*amino*-1-*o*-*tolyl*-3-*methylpyrazole methiodide*, $CH\!\!<\!\!\begin{matrix} C(NH_2) \cdot N \cdot C_7H_7 \\ CMe\text{---}NMeI \end{matrix}$, m. p. 245°, colourless crystals, by boiling methyl alcoholic methyl iodide. The methiodide is changed by silver chloride to the *methochloride*, m. p. 241°, an aqueous solution of which yields, by treatment with concentrated sodium hydroxide, 2 : 5-*imino*-1-*o*-*tolyl*-2 : 3-*dimethylpyrazole* (1-*o*-*tolyl*-

iminopyrine), $\mathrm{C}\!\!\Big\langle\!\!\begin{array}{c}\mathrm{CH\cdot CMe}\\[-2pt]\mathrm{-NH-}\\[-2pt]\mathrm{N(C_7H_7)}\end{array}\!\!\Big\rangle\!\mathrm{NMe}$, m. p. 35—36°, yellow crystals,

from which have been prepared the *carbonate*, m. p. 98° (decomp.), *picrate*, m. p. 165°, yellow needles, *benzenesulphonyl* derivative,

$$\mathrm{C_{18}H_{19}O_2N_3S},$$

m. p. 179°, *benzoyl* derivative, m. p. 186°, and 4-*benzeneazo*-1-*o*-*tolyl-iminopyrine*, $\mathrm{C_{18}H_{19}N_5}$, m. p. 188°, yellowish-brown leaflets.
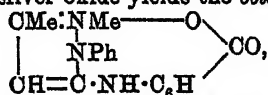
The following compounds of the para-series are prepared by methods similar to the preceding: *Acetoacetonitrile*-p-*tolylhydrazone*, m. p. 123°, yellow leaflets; 5-*amino*-1-p-*tolyl*-3-*methylpyrazole*, m. p. 120°, colourless needles; 4-*bromo*-5-*amino*-1-p-*tolyl*-3-*methylpyrazole*, m. p. 128°, colourless needles; 4-*bromo*-1-p-*tolyl*-3-*methyl*-4:5-*azipyrazole*, m. p. 103°, orange-red leaflets; 4-*oximino*-5-*imino*-1-p-*tolyl*-3-*methyl-pyrazolone*, m. p. 198°, bordeaux-red crystals; 5-*amino*-1-p-*tolyl*-3-*methylpyrazole methiodide*, m. p. 135°, and *methochloride*; 1-p-*tolyl-iminopyrine* (*picrate*, m. p. 177°, yellow needles; *benzenesulphonyl* derivative, m. p. 203°; *carbonate*, decomp. 126°; and 4-*benzeneazo*-derivative, m. p. 191°, yellowish-brown leaflets).　　　C. S.

5-p-Carboxylic Acids of Anilopyrine and their Esters. August Michaelis and Wilhelm Titius (*Annalen*, 1913, **397**, 159—180).— The main object of the research is the production of further evidence in support of Michaelis's constitution for the iminopyrines. Antipyrine chloride and methyl p-aminobenzoate (3 mols.), heated at 130°, yield, by basifying the aqueous solution of the product, *methyl* 2:5-*anilo*-1-*phenyl*-2:3-*dimethylpyrazole*-p-*carboxylate* (*methyl anilopyrine*-p-*carboxylate*),

$$\mathrm{C\!\!\begin{array}{c}\mathrm{OMe\colon\!NMe}\\ |\qquad\quad\;\;\mathrm{NPh}\\ \mathrm{CH=\!C}\end{array}\!\!\!\!\Big\rangle N\cdot C_6H_4\cdot CO_2Me},$$ m. p. 155°, greenish-yellow prisms,

which forms a *hydrochloride*, m. p. 142°, *platinichloride*, m. p. 200°, red crystals. *hydriodide*, m. p. 212° (decomp.), colourless needles, and *methiodide*, $\mathrm{C_{20}H_{22}O_2N_3I,3H_2O}$, m. p. 102° (anhydrous, 202° [decomp.]), and is converted into the 4-bromo-compound, $\mathrm{C_{19}H_{18}O_2N_3Br}$, m. p. 170°, yellow leaflets, by bromine in acetic acid. By hydrolysing the ester with concentrated alcoholic potassium hydroxide and treating the product with hydrochloric acid and finally with aqueous potassium iodide, the *hydriodide*, m. p. 236°, colourless needles, of anilopyrine-p-carboxylic acid is obtained. According to the authors, it has the

constitution $\mathrm{CO_2H\cdot C_6H_4\cdot NH\cdot C\!\!\begin{array}{c}\mathrm{NPh\cdot NMeI}\\ \!\!\big\langle\quad\;\;\|\\ \mathrm{CH-CMe}\end{array}}$, and by treating its

aqueous solution with silver oxide yields the *betaine*,

$$\mathrm{C\!\!\begin{array}{c}\mathrm{OMe\colon\!NMe\!-\!-\!O}\\ |\qquad\quad\;\mathrm{NPh}\qquad\;\big\rangle CO,\\ \mathrm{CH=\!C\cdot NH\cdot C_6H}\end{array}}$$

which crystallises in needles containing $5\mathrm{H_2O}$, m. p. 99—100° (the anhydrous substance is yellow and has m. p. about 150°), has a neutral reaction in dilute aqueous or alcoholic solution and a distinctly alkaline reaction in concentrated solution, does not form salts

with bases, but does so readily with acids (*hydrochloride*, $C_{18}H_{17}O_2N_3, HCl$; *platinichloride*, $2C_{18}H_{17}O_2N_3, H_2PtCl_6$, m. p. 217°, golden-yello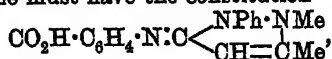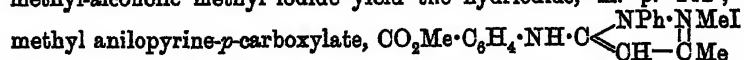w crystals), and, although soluble in aqueous alkalis, is precipitated therefrom by carbon dioxide. If iminopyrine has the constitution,

$$NPh<\begin{matrix} C(:NH)\cdot CH \\ | \quad\quad || \\ NMe\!-\!-\!CMe \end{matrix}$$. ascribed to it by Roser and Stolz (A., 1904, i, 113),
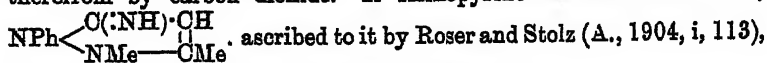
the preceding betaine must have the constitution

$$CO_2H\cdot C_6H_4\cdot N\!:\!C<\begin{matrix} NPh\cdot NMe \\ CH\!=\!CMe \end{matrix}'$$

and therefore should exhibit acid properties. The betaine and methyl-alcoholic methyl iodide yield the hydriodide, m. p. 212°, of

methyl anilopyrine-*p*-carboxylate, $CO_2Me\cdot C_6H_4\cdot NH\cdot C<\begin{matrix} NPh\cdot NMeI \\ CH\!-\!CMe \end{matrix}$.

By evaporating a hydrochloric acid solution of methyl anilopyrine-*p*-carboxylate and heating the residue under reduced pressure, methyl chloride is evolved, and the product, after treatment with sodium hydroxide, yields 5-anilo-1-phenyl-3-methylpyrazolone. This substance is produced by the decomposition of the initially-formed *5-anilo-1-phenyl-3-methylpyrazolone-p-carboxylic acid*, $CO_2H\cdot C_6H_4\cdot N\!:\!C<\begin{matrix} NPh\cdot N \\ CH_2\!-\!CMe \end{matrix}'$ colourless needles containing H_2O, m. p. 114° (the anhydrous substance, m p. 140—150° [decomp.], is yellow).

Methyl 5-methylanilino-1-phenyl-3-methylpyrazole-p-carboxylate (*methyl ψ-anilopyrine-p-carboxylate*), $CO_2Me\cdot C_6H_4\cdot NMe\cdot C<\begin{matrix} NPh\cdot N \\ CH\!-\!CMe \end{matrix}'$, m. p. 132°, colourless needles, is obtained by heating the methiodide of methyl anilopyrine-*p*-carboxylate at 200° under reduced pressure. It is converted into the 4-*nitroso*-compound, $C_{19}H_{18}O_3N_4$, m. p. 151°, pale green leaflets, by sodium nitrite and glacial acetic acid containing a few drops of hydrochloric acid, into the 4-*nitro*-compound, $C_{19}H_{18}O_4N_4$, m. p. 170°, pale yellow needles, by nitric acid, into a *dibromo*-derivative, $C_{19}H_{17}O_2N_3Br_2$, m. p. 115°, by bromine on the water-bath, and into the corresponding *acid*, $C_{18}H_{17}O_2N_3$, m. p. 193°, by hydrolysis. This acid is isomeric with the betaine mentioned previously, but exhibits pronounced acid reaction and properties, being soluble in dilute alkali hydroxides and carbonates and in ammonia; the crystalline *barium* salt, $Ba(C_{18}H_{16}O_2N_3)_2$, is described.

Ethyl 2:5-anilo-1-phenyl-2:3-dimethylpyrazole-p-carboxylate (*ethyl anilopyrine-p-carboxylate*), $C_{20}H_{21}O_2N_3$, m. p. 76°, greenish-yellow, fluorescent crystals, is prepared in the same manner as the methyl ester. It forms a *hydriodide*, $CO_2Et\cdot C_6H_4\cdot NH\cdot C<\begin{matrix} NPh\cdot NMeI \\ CH\!-\!CMe \end{matrix}$ yellow crystals containing H_2O, m. p. 110—111°, *methiodide*,

$$CO_2Et\cdot C_6H_4\cdot NMe\cdot C<\begin{matrix} NPh\cdot NMeI \\ CH\!-\!CMe \end{matrix}'$$
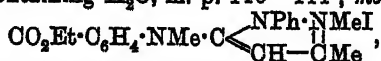
colourless crystals containing 3H_2O, m. p. 80° (anhydrous, 183°), and *ethiodide*, $C_{22}H_{26}O_2N_3I$, m. p. 176°, colourless needles, and by hydrolysis yields the same betaine as the methyl ester.

By heating the methiodide of the ethyl ester at 160—180° under re-

duced pressure, *ethyl 5-methylanilino-1-phenyl-3-methylpyrazole-p-carboxyl-ate* (*ethyl ψ-anilopyrine-p-carboxylate*), $CO_2Et \cdot C_6H_4 \cdot NMe \cdot C \underset{CH—CMe'}{\overset{NPh \cdot N}{<}}$
m. p. 105°, colourless needles, is obtained, by the hydrolysis of which ψ-anilopyrine-*p*-carboxylic acid, m. p. 193°, is obtained.

In a similar manner the ethiodide of the ethyl ester yields *ethyl 5-ethylanilino-1-phenyl-3-methylpyrazole-p-carboxylate*, m. p. 95°, colourless needles.   C. S.

Synthesis of Herzynine. R. ENGELAND and FRIEDRICH KUTSCHER (*Chem. Zentr.*, 1913, i, 28—29 ; from *Zentr. Physiol.*, 1912, **26**, 569—570. Compare A., 1911, ii, 528).—The substance, $C_9H_{15}O_2N_3$, which was isolated from mushrooms in the form of the aurichloride, has been identified with trimethylhistidine. This base is prepared by treating histidine hydrochloride in concentrated hydrochloric acid with silver nitrite and warming the syrup obtained by evaporating the filtrate with an alcoholic solution of trimethylamine, when the base is precipitated by phosphotungstic acid, converted into the chloride, then into the platinichloride, and finally into the *aurichloride*,

$$C_9H_{17}O_2N_3Au_2Cl_8,$$

m. p. 183° (decomp.). The direct methylation of histidine affects the glyoxaline ring, and, under certain conditions, a good yield of *penta-methylhistidine* may be obtained as an unstable base which forms a stable chloride and a sparingly soluble *aurichloride*, $C_{11}H_{21}O_2N_3Au_2Cl_8$, m. p. 220°, but does not respond to the diazo-reaction.   J. C. W.

The Identity of Trimethylhistidine (Histidine-betaine) from Various Sources. GEORGE BARGER and ARTHUR J. EWINS (*Biochem. J.*, 1913, **7**, 204—206).—Proof is given of the identity of the histidine-betaine described by the author (T., 1911, **99**, 2336) with the compounds obtained by Reuter and Kutscher. The difference in the m. p. given for the dipicrate is due to this substance melting at 123—124° when hydrated ($2H_2O$) and at 205—206° when anhydrous. The dipicrate has m. p. 213°; the monopicrate, m. p. 201—202°. The aurichloride of betaine has m. p. 184°, not at 171° as previously stated. Histidine-betaine has $[\alpha]_D + 46 \cdot 5°$.   W. D. H.

Synthetical Alkaloids from Tyrosine, Tryptophan and Histidine. JULIUS WELLISCH (*Biochem. Zeitsch.*, 1913, **49**, 173—194).—The author discusses the mechanism of the various processes by means of which physiologically active bases can be synthesised in plants, especially from amino-acids which can be derived from the hydrolysis of proteins. Amongst these may be reckoned in the first instances, bases such as 3-β-aminoethylglyoxaline, 3-β-aminoethylindole, and phenylethylamine, which are derived from histidine, tryptophan, and phenylalanine by the simple scission of carbon dioxide. Another important series derivable from these amino-acids are the quinoline and pyridine derivatives, which can be obtained from the acids or the corresponding amines by condensation with aldehydes, such as formaldehyde, and subsequent ring formation. Attempts have been

made to prepare a series of alkaloids by the latter method. By the condensation of histidine with formaldehyde, which was carried out by heating the base with methylal and hydrochloric acid, *tetrahydro-1 : 3 : 5-benzotriazole-6-carboxylic acid*, $C_7H_9N_3O_2,2HCl$, in the form of its *hydrochloride*, m. p. 278° (corr.), was obtained. The *picrate* decomposes about 215°. The hydrochloride is lævorotatory ($[a]_D^{25} = -84\cdot24°$ by the micropolarisation method). On heating in a vacuum to 290°, carbon dioxide is evolved, and the corresponding *iminazole-isopiperidine [tetrahydro-1 : 3 : 5-benzotriazole] hydrochloride*,

$$C_6H_9ON_3,2HCl,$$

which decomposes at 258°, was obtained, and which separates from alcohol in a microcrystalline form. The carboxylic acid cannot be esterified by alcohol and hydrochloric acid, and only with very great difficulty by the action of ethyl iodide on the silver salt. Attempts were made ty obtain a corresponding product by the action of methylal on tryptophan, but a pure substance was not isolated. *l*-Tyrosine under similar conditions gives 7-hydroxytetrahydro*iso*quinoline-3-carboxylic acid (Pictet and Spengler, A , 1911, i, 750), which has $[a]_D^{25} = -45\cdot62°$ in hydrochloric acid. This on heating in a vacuum appears to be converted into an anhydride. The *ethyl* ester and its *picrate* were also prepared. Attempts to condense histidine with acetaldehyde and pyruvic acid did not lead to the isolation of pure products.

S. B. S.

Derivatives of *iso*Cinchomeronic Acid and 2 : 5-Diaminopyridine. HANS MEYER and FRIEDRICH STAFFEN (*Monatsh.*, 1913, 34, 517—533).—Very few derivatives of *iso*cinchomeronic acid (pyridine-2 : 5-dicarboxylic acid) have been described (compare Weidel and Herzig, A., 1886, 477 ; Meyer, A., 1903, i, 364).

*iso*Cinchomeronic acid was obtained for this investigation by the condensation of aldehyde ammonia with twice its weight of paraldehyde in an autoclave at 220—230°, and oxidation of the resultant 2 : 5-methylethylpyridine with the theoretical amount of potassium permanganate. The m. p. of the acid can be raised from 237° to 254° (decomp.) by conversion into the methyl ester and regeneration ; ammonium salt, m. p. 153°. If the acid is heated with excess of thionyl chloride, it is converted into iso*cinchomeronyl chloride*,

$$C_5NH_3(COCl)_2,$$
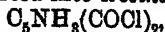
needles, m. p. 59°, which reacts with methyl alcohol in the cold, producing *methyl* iso*cinchomeronate*, needles, m. p. 164°, which is also obtainable by heating a mixture of the acid and alcohol with sulphuric acid at 100°. The acid chloride in the cold and the methyl ester at 100° react with ammonia solution, forming iso*cinchomeronamide*, $C_5NH_3(CO\cdot NH_2)_2$, colourless crystals, m. p. 310° (decomp.). When boiled in alcoholic solution with an equal weight of hydrazine hydrate, methyl *iso*cinchomeronate is converted into a crystalline solid, from which chloroform extracts the *methyl* ester of iso*cinchomeronic acid hydrazide*, $C_5NH_3(CO_2Me)\cdot CO\cdot NH\cdot NH_2$, yellow scales, m. p. 173° (decomp.), whilst the undissolved residue consists of iso*cinchomerono-hydrazide*, $C_5NH_3(CO\cdot NH\cdot NH_2)_2$, prismatic needles, m. p. 268—269°

(decomp.), with rapid heating, which is obtained in almost theoretical yield if twice the above proportion of hydrazine hydrate be used in the preparation. The dihydrazide condenses with various aldehydes when heated with them, or when shaken in aqueous solution with them; isocinchomeronodibenzylidenehydrazide, colourless needles, m. p. 290°; isocinchomeronodi-o-chlorobenzylidenehydrazide, colourless leaflets, m. p. 308° (decomp.); isocinchomeronodi-4-hydroxy-3-methoxybenzylidene-hydrazide, a yellow, crystalline substance, m. p. 264—266°, which is turned red on the addition of mineral acids. An aqueous solution of the dihydrazide containing the theoretical quantity of hydrochloric acid reacts with sodium nitrite, giving a precipitate of isocinchomerono-diazoimide, $C_5NH_3(CO \cdot N_3)_2$, colourless prisms, m. p. 114° (decomp. with explosion), together with a small amount of an acid substance, a colourless, crystalline powder, m. p. 307° (decomp.), which from its reaction with ferrous sulphate is a 2-substituted pyridine derivative. The carefully-dried hydrazide when boiled with alcohol first dissolves and then gives a deposit of ethylurethylpyridylazoimide,

$$N_3 \cdot CO \cdot C_5NH_3 \cdot NH \cdot CO_2Et,$$
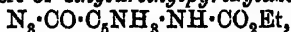
colourless needles, m. p. 153° (with explosion), which by prolonged treatment with boiling alcohol is further converted into 2 : 5-diethyl-urethylpyridine, $C_5NH_3(NH \cdot CO_2Et)_2$, colourless needles, m. p. 198—199°, the ethoxyl groups of which, unlike those of the corresponding derivative of dipicolinic acid, are easily removed by hydriodic acid. The corresponding methylurethylpyridylazoimide,

$$N_3 \cdot CO \cdot C_5NH_3 \cdot NH \cdot CO_2Me,$$
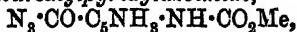
and 2 : 5-dimethylurethylpyridine form colourless needles (which explode at 80—100° if rapidly heated, and melt at above 270° with decomp. if heated slowly) and colourless needles, m. p. 206—207° (decomp.) respectively.

If the above diethylurethylpyridine is boiled for three hours with hydriodic acid (D 1·8—1·9), yellow needles and leaflets of the hydriodide of 2 : 5-diaminopyridine separate on cooling ; the free base, colourless needles, m. p. 107—110°, which is rapidly affected by air and light, can be isolated by triturating the hydriodide with crushed potassium carbonate and carefully extracting with hot benzene in an atmosphere of carbon dioxide. By the action of silver chloride the hydriodide is converted into the hydrochloride, colourless needles, which, like the free base, gives solutions in water and alcohol with a blue fluorescence ; the unstable platinichloride crystallises in golden-yellow scales ; benzoyl derivative, colourless needles, m. p. 229—230°. The base does not possess the usual properties of an aromatic para-diamine ; it gives an intense reddish-yellow coloration with ferric chloride, and the hydrochloride reduces gold solutions and ammoniacal silver solutions.   D. F. T.

Preparation of Acylacetic Esters. ANDRÉ WAHL and M. DOLL (*Bull. Soc. chim.*, 1913, [iv], **13**, 265—281. Compare A., 1911, i, 108).—The authors have continued their previous work on the condensation of ethyl acetate with its higher homologues by means of sodium, and have improved the yields by suitable modification of the

procedure, which is fully described.   They have also extended the method to the cases of ethyl valerate and ethyl heptoate, and find that the yield of ketonic ester increases with increasing length of the carbon chain of the ester provided the latter is normal.   With esters having side-chains, condensation is effected with greater difficulty.

Ethyl propionylacetate has now been obtained in 13% yield.   It forms a green *copper* salt, m. p. 144°.

Ethyl butyrylacetate is readily converted into *ethyl isonitrosobutyryl-acetate*, which did not solidify even after several months and could not be distilled without decomposition.   Phenylhydrazine converts it into *4-oximino-1-phenyl-3-propyl-5-pyrazolone*, yellow needles, m. p. 128°.   When acted on by benzenediazonium chloride, ethyl butyrylacetate is converted into a yellow *oil*, which is identified as ethyl phenylazo-butyrylacetate, since it is converted by phenylhydrazine into *4-phenyl-hydrazino - 1-phenyl - 3 - propyl- 5 -pyrazolone*, $NPh<\begin{smallmatrix}CO{-}C{:}N{\cdot}NHPh\\ N{=\!=}CPr\end{smallmatrix}$, orange needles, m. p. 133—134°, and by *p*-nitrophenylhydrazine into *4-phenylhydrazino-1-p-nitrophenyl-3-propyl-5-pyrazolone*, golden-yellow needles, m. p. about 209—210°.   *Ethyl p-nitrophenylazobutyrylacetate* crystallises in fine yellow needles, m. p. 101°, whilst the corresponding *acid*, prepared by saponification of the ester with cold alcoholic sodium hydroxide and subsequent addition of acid, forms yellow crystals, m. p. 164°.   *4-p-Nitrophenylhydrazino-1-phenyl-3-propyl-5-pyrazolone*, $NPh<\begin{smallmatrix}CO{-}C{:}N{\cdot}NH{\cdot}C_6H_4NO_2\\ N{=\!=}CPr\end{smallmatrix}$, red needles, m. p. 194°, 4-p-*nitro-phenylhydrazino-1-p-nitrophenyl-3-propyl-5-pyrazolone*, orange needles, m. p. 243—244°, and *4-p-nitrophenylhydrazino-1-tolyl-3-propyl-5-pyra-zolone*, orange needles, m. p. 152°, were also prepared.

Ethyl valerylacetate, $CH_2Pr{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$, b. p. 110—112°/16 mm. (compare Blaise and Luttringer, *Bull. Soc. chim*, 1905, [iii], **33**, 1103), is obtained in 28% yield.   It gives a *copper* salt, green needles, m. p. 91°, which, when boiled with methyl alcohol, is converted into a blue basic *salt*, $C_9H_{15}O_3{\cdot}CuOMe$, m p. 80°.   It is transformed by hydrazine hydrate into *3-n-butylpyrazolone*, white leaflets, m. p. 197°.

Ethyl *iso*valerate reacts slowly with ethyl acetate with the formation of poor yields of *ethyl isovalerylacetate*, b. p. 96—99°/14 mm.   The latter gives a green normal *copper* salt, m. p. 122°, which when boiled with methyl alcohol forms indigo-blue crystals of the basic *salt*,

$$C_9H_5O_3{\cdot}CuOMe,$$
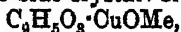
m. p. 106—107°.

Ethyl heptoylacetate, b. p. 123—126°/11 mm. (compare Moureu and Delange, A., 1903, i, 676), is obtained in 40% yield by the condensation of ethyl heptoate with ethyl acetate.   The following new compounds have been prepared from it : *4-phenylhydrazino-1-phenyl-3-hexyl-5-pyrazolone*, orange-yellow needles, m. p. 100—101° ; *4-p-nitrophenyl-hydrazino-1-p-nitrophenyl-3-hexyl-5-pyrazolone*, orange needles, m. p. 192° ; *1-phenyl-3-hexyl-5-pyrazolone*, nearly white leaflets, m. p. 83—84°, formed by heating at its b. p. for a few moments an acetic acid solution of molecular quantities of the ketonic ester and phenylhydrazine.   If

CH$_3$·[CH$_2$]$_5$·C—CH—CH—C·[CH$_2$]$_5$·CH$_3$

N CO   CO N

NPh   NPh

(I.)

CH$_3$·[CH$_2$]$_5$·C—C≡C—C·[CH$_2$]$_5$·CH$_3$

N CO CO N

NPh   NPh

(II.)
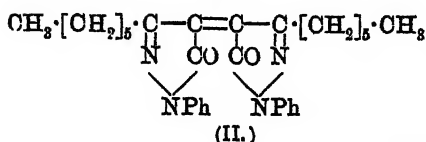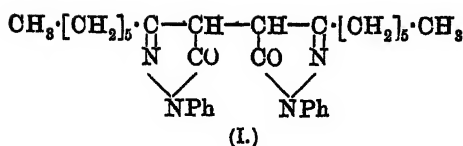
in the latter case 2 to 3 molecules of phenylhydrazine are employed for each molecule of ketonic ester, 1-*phenyl*-3-*hexylbispyrazolone* (formula I), crystalline powder, m. p. 276—278° (decomp.), is obtained, which, when heated in alkaline solution with sodium nitrite and subsequently acidified, yields the compound (formula II) crystallising in blue needles, m. p. 145°.

The method has also been successfully applied to certain cyclic esters. Ethyl benzoate and ethyl acetate gave ethyl benzoylacetate in 80% yield (compare Wahl, A., 1908, i, 647; Wahl and Silberzweig, A., 1912, i, 114), whilst the corresponding methyl ester gave an 85% yield of methyl benzoylacetate. *Propyl benzoylacetate*, prepared by boiling methyl benzoylacetate with propyl alcohol in a fractionating apparatus so arranged that the displaced methyl alcohol slowly distils, forms an amber liquid, b. p. 154—156°/12 mm., D⁰ 1·114. The normal *copper* salt forms green leaflets, m. p. 145—146°, whilst the basic *salt*, $C_{12}H_{13}O_3$·CuOMe, consists of blue crystals, m. p. 195°.

The normal green *copper* salt, m. p. 133°, of *iso*butyl benzoylacetate is decomposed by boiling methyl alcohol with formation of the bluish-grey basic *salt*, $C_{13}H_{15}O_3$·CuOMe, m. p. 191°, and by boiling ethyl alcohol into the blue basic *salt*, $C_{13}H_{15}O_3$·CuOEt, m. p. 188°.

Under the conditions used in the preparation of the benzoylacetates, a 60% yield of methyl o-methoxybenzoylacetate and a 62% yield of methyl anisoylacetate were obtained. The yield of ethyl furoylacetate was 76% of the theoretical (compare Torrey and Zanetti, A., 1907, i, 146; 1908, i, 840; 1910, i, 892).   H. W.

[Preparation of an Anthracene Derivative.] CHEMISCHE FABRIK GRIESHEIM - ELEKTRON (D.R.-P. 255641).—The *compound* (annexed formula) is obtained when pyrazoleanthrone (A., 1906, i, 904) is boiled with potassium hydroxide (5 parts) and alcohol (10 parts) until the so-obtained blue colour ceases to gain intensity.
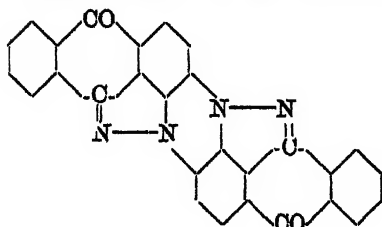
F. M. G. M.

New Derivatives of Azoxybenzene. ANGELO ANGELI and BRUNO VALORI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 132—140. Compare A., 1912, i, 321).—*p*-Azobenzenecarboxylic acid (which has m. p. 241°)

is conveniently prepared from p-aminobenzoic acid and nitrosobenzene When it is treated in acetic acid solution with hydrogen peroxide, β-*azoxybenzenecarboxylic acid*, $NPh{:}NO{\cdot}C_6H_4{\cdot}CO_2H$, is obtained; it crystallises in yellow needles, m. p. 241°. Its *ethyl* ester, $C_{15}H_{14}O_3N_2$, has m. p. 68°. The acid yields p-azobenzenecarboxylic acid on reduction. When it is treated with bromine in the presence of iron filings, p-*bromo*-β-*azoxybenzenecarboxylic acid*, $C_{13}H_9O_3N_2Br$, is produced; it is a yellowish-white, crystalline powder, m. p. 280°. The *ethyl* ester of this acid, $C_{15}H_{13}O_3N_2Br$, has m. p. 114°. When β-azoxybenzenecarboxylic acid is nitrated in glacial acetic acid solution, p-*nitro*-β-*azoxybenzenecarboxylic acid*, $C_{13}H_9O_5N_3$, is obtained as a yellow, crystalline powder, m. p. about 260° with evolution of gas. If kept for an hour on the water-bath with excess of concentrated sulphuric acid, β-azoxybenzenecarboxylic acid undergoes rearrangement, yielding 4-*hydroxyazobenzene*-4'-*carboxylic acid*, $HO{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}CO_2H$, which forms red crystals, m. p. 266° (decomp.).

a-*Azoxybenzenecarboxylic acid*, $O{:}NPh{:}N{\cdot}C_6H_4{\cdot}CO_2H$, is formed in the preparation of the β-acid, and can be separated from it by reason of its greater solubility in acetic acid. It is also obtained by the action of chromic acid on the β-compound It forms pale yellow scales, m. p. 231°. Its *ethyl* ester, $C_{15}H_{14}O_3N_2$, has m. p. 77·5°. The a-acid is not acted on by bromine. On reduction with aluminium amalgam, it yields p-azobenzenecarboxylic acid.

β-p-*Azoxybenzenesulphonic acid*, $C_{12}H_{10}O_4N_2S$, prepared by the action of hydrogen peroxide on p-azobenzenesulphonic acid, forms pale yellow needles, m. p. 144°. The *silver* salt, $C_{12}H_9O_4N_2SAg$, crystallises in lustrous laminæ. The acid described under the name of p-azoxybenzenesulphonic acid by Limpricht (A., 1885, 984) cannot have this structure. β-p-Azoxybenzenesulphonic acid yields a bromo-derivative, p-*bromo*-β-*azoxybenzenesulphonic acid*, $C_{12}H_9O_4N_2SBr$, which does not melt at 280°. β-p-Azoxybenzenesulphonic acid suffers the Wallach rearrangement, yielding a red, crystalline powder, $C_{12}H_{10}O_4N_2S$, which blackens about 200°, but does not melt.

a-2 : 4 : 6:*Trinitroazoxybenzene*, $O{:}NPh{:}N{\cdot}C_6H_2(NO_2)_3$, is obtained in long, pale yellow needles, m. p. 170°, by the action of hydrogen peroxide on trinitroazobenzene. This substance dissolves unaltered in nitric acid (D 1·45) and in bromine, but when it is dissolved in nitric acid of D 1·52, and the solution kept for twelve hours, it yields a *tetranitro*-derivative, $C_{12}H_9O_9N_6$, which forms yellow prisms, m. p. 192°.   R. V. S.

Diazo-compounds derived by the Action of Alkali on Nitrosophthalimidine. Simplified Preparation of Nitrosophthalimidine. ALFRED OPPE (*Ber.*, 1913, **46**, 1095—1099).— Aqueous alkali transforms nitrosophthalimidine into o-hydroxymethylbenzoic acid or its lactone (Graebe, A., 1889, 140), diazo-compounds being probably formed as intermediate products. The isolation of the latter has been accomplished by substituting absolute methyl-alcoholic sodium methoxide for aqueous alkali hydroxide in opening the lactam ring.

When a solution of sodium methoxide in absolute methyl alcohol

is added to a well-cooled suspension of nitrosophthalimidine in dry ether, a micro-crystalline salt separates, analysis of which gives results intermediate between those required for the *salt diazoxide*,

$$CO_2Na \cdot C_6H_4 \cdot CH_2 \cdot N_2 \cdot ONa,$$
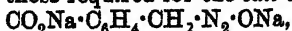
and the *ester diazoxide*, $CO_2Me \cdot C_6H_4 \cdot CH_2 \cdot N_2 \cdot ONa$. The former could be obtained in the pure state by pouring the freshly-prepared reaction mixture into a large quantity of cooled ether, but the latter could not be obtained pure. When the above reaction mixture is treated with dry carbon dioxide before the separation of crystals occurs, *methyl o-diazomethylbenzoate*, $CO_2Me \cdot C_6H_4 \cdot CH \colon N_2$, needles, m. p. 34°, is obtained, which is readily decomposed by phenol with quantitative evolution of nitrogen and formation of *methyl o-phenoxymethylbenzoate*, $CO_2Me \cdot C_6H_4 \cdot CH_2 \cdot OPh$, needles, m. p. 52·5°, b. p. 204°/13 mm. The corresponding free *acid* crystallises in needles, m. p. 126°, and is decomposed by fuming hydrochloric acid at 170—180° into phenol and *o*-hydroxymethylbenzoic acid. The latter is converted by heat into phthalide, leaflets, m. p. 73°.

The following process is recommended for the preparation of nitrosophthalimidine. Nearly boiling 25% hydrochloric acid is gradually added to a paste made by grinding phthalimide and zinc dust with a small quantity of water. The mixture is maintained at its boiling point until there is no further action on the zinc, filtered, cooled, and treated with a concentrated aqueous solution of sodium nitrite. In this manner, 100 grams of phthalimide yield 75 grams of nitrosophthalimidine.   H. W.

Etherification of *o*-Hydroxyazo-compounds. II. G. CHARRIER and G. FERRERI (*Atti R. Accad. Sci. Torino*, 1913–13, 48, 539—556. Compare A., 1912, i, 812).—1-*Benzeneazo-2-naphthyl ethyl ether*, $OEt \cdot C_{10}H_6 \cdot N \colon NPh$, forms garnet-red tablets, m. p. 79°; in its preparation 50% potassium hydroxide is used instead of 30% sodium hydroxide. When the substance is reduced with zinc and acetic acid, aniline and 1-amino-2-naphthyl ethyl ether are produced. The *hydrochloride*, $C_{18}H_{16}ON_2, 2HCl$, crystallises in heavy, green leaflets, which have a metallic lustre. The *hydrobromide* is a coffee-coloured, crystalline powder. The hydriodide is a heavy, dark coffee-coloured, crystalline powder.

1-*o*-*Tolueneazo-2-naphthyl ethyl ether*, $OEt \cdot C_{10}H_6 \cdot N \colon N \cdot C_6H_4Me$, crystallises in garnet-red, flattened needles, m. p. 36°. It dissolves in concentrated sulphuric acid, giving a red coloration, and dissolves also in dilute acids, forming red solutions. The *hydrochloride*,

$$C_{19}H_{18}ON_2, 2HCl,$$
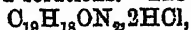
crystallises in needles with a green, metallic lustre.

1-*m*-*Tolueneazo-2-naphthyl methyl ether*, $OMe \cdot C_{10}H_6 \cdot N \colon N \cdot C_6H_4Me$, forms garnet-red, tabular crystals, m. p. 81°. The *hydrochloride* forms minute, red crystals with a golden lustre.

1-*m*-*Tolueneazo-2-naphthyl ethyl ether*, $OEt \cdot C_{10}H_6 \cdot N \colon N \cdot C_6H_4Me$, crystallises in red leaflets, m. p. 84°. The *hydrochloride* is a heavy, coffee-coloured substance.

1-*p*-*Tolueneazo-2-naphthyl ethyl ether*, $OEt \cdot C_{10}H_6 \cdot N \colon N \cdot C_6H_4Me$, crys-

tallises in red, prismatic needles, m. p. 48°. The *hydrochloride*, $C_{10}H_{18}ON_2,2HCl$, forms reddish-brown needles with a golden lustre.
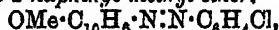
1-m-*Chlorobenzeneazo-2-naphthyl methyl ether*,
$$OMe \cdot C_{10}H_6 \cdot N \vdots N \cdot C_6H_4Cl,$$
crystallises in bright red prisms or needles, m. p. 77°. The *hydrochloride* forms red needles.

1-m-*Chlorobenzeneazo-2-naphthyl ethyl ether*, $OEt \cdot C_{10}H_6 \cdot N \vdots N \cdot C_6H_4Cl$, forms red needles, m. p. 35°. The *hydrochloride* forms dark garnet-red crystals with a golden lustre.

1-p-*Chlorobenzeneazo-2-naphthyl methyl ether*,
$$OMe \cdot C_{10}H_6 \cdot N \vdots N \cdot C_6H_4Cl,$$
crystallises in shining red needles, m. p. 65°. The *hydrochloride*, $C_{17}H_{13}ON_2Cl,2HCl$, is a red, crystalline substance.

1-p-*Chlorobenzeneazo-2-naphthyl ethyl ether*, $OEt \cdot C_{10}H_6 \cdot N \vdots N \cdot C_6H_4Cl$, crystallises in red needles with a golden lustre, m. p. 53°. The *hydrochloride* is a reddish-brown, crystalline powder.
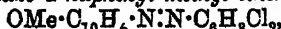
1-op-*Dichlorobenzeneazo-2-naphthyl methyl ether*,
$$OMe \cdot C_{10}H_6 \cdot N \vdots N \cdot C_6H_3Cl_2,$$
forms garnet-red leaflets, m. p. 98°. The *hydrochloride* is a red, crystalline powder having a metallic lustre.
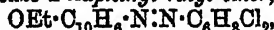
1-op-*Dichlorobenzeneazo-2-naphthyl ethyl ether*,
$$OEt \cdot C_{10}H_6 \cdot N \vdots N \cdot C_6H_3Cl_2,$$
separates in garnet-red needles, m. p. 102°. The *hydrochloride* forms minute, reddish-brown crystals with a metallic lustre.
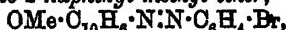
1-m-*Bromobenzeneazo-2-naphthyl methyl ether*,
$$OMe \cdot C_{10}H_6 \cdot N \vdots N \cdot C_6H_4 \cdot Br,$$
crystallises in ruby-red needles, m. p. 92°. The *hydrochloride* is a red, crystalline substance having a metallic lustre.

1-m-*Bromobenzeneazo-2-naphthyl ethyl ether*, $OEt \cdot C_{10}H_6 \cdot N \vdots N \cdot C_6H_2 \cdot Br$, forms crusts of golden-yellow needles, m. p. 52°. The *hydrochloride* crystallises in metallic-looking, green leaflets.

The m. p. of 1-p-methoxybenzeneazo-2-naphthylethylether is 55—56°, not 52—53°, as stated in the former paper. The *hydrochloride* of the ether is a reddish-brown, crystalline powder having a green metallic lustre.
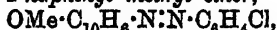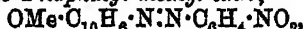
1-m-*Nitrobenzeneazo-2-naphthyl methyl ether*,
$$OMe \cdot C_{10}H_6 \cdot N \vdots N \cdot C_6H_4 \cdot NO_2,$$
crystallises in small, red needles, m. p. 94—95°. The *hydrochloride* is a red, crystalline substance, as also is the *hydrobromide*.

1-m-*Nitrobenzeneazo-2-naphthyl ethyl ether*, $OEt \cdot C_{10}H_6 \cdot N \vdots N \cdot C_6H_4 \cdot NO_2$, forms garnet red needles, m. p. 106—107°. The *hydrochloride* is a red, crystalline powder.

The salts of these ethers are to be assigned the constitutions indicated by the following formula:
$$\begin{array}{c} R \\ Cl \end{array} \!\!\! \diagdown \!\!\! \begin{array}{c} \\ \diagup \end{array} O \cdot C_{10}H_6 \cdot N \vdots N \!\!\! \diagup\!\!\!\diagdown \!\!\! \begin{array}{c} Ar \\ Cl \\ H \end{array}.$$

R. V. S.

Hydroxyazo-compounds and Quinonephenylhydrazones of the Anthracene Series.

KURT H. MEYER and KARL ZAHN (*Annalen*, 1913, **396**, 152—166).—Benzeneazoanthranol, identical with the substance obtained by Kaufler and Suchanek by the con-

densation of benzenediazonium chloride and anthranol, is prepared by treating 9 : 9-dibromoanthrone with alcoholic phenylhydrazine; only the one substance is produced at − 10° or at the b. p., or by working in other solvents. The same substance also is immediately recovered when the deep blue solution of benzeneazoanthranol in alcoholic potassium hydroxide is added to sulphuric acid at 0°. No evidence of the existence of the parent substance as anthraquinonephenylhydrazone has been obtained. Benzeneazoanthranol yields differently coloured solutions in different solvents, develops a deep brown coloration with concentrated sulphuric acid, forms coloured additive compounds with stannic chloride and aluminium chloride, reacts instantly with alcoholic bromine, and is stable to boiling acetic acid ; it is hydrolysed by 5% alcoholic sulphuric or hydrochloric acid after boiling for seven hours. All these properties, except variability of colour in solution, are also characteristic of *benzeneazoanthranyl benzoate*,

$$\text{NPh:N·C}\!\!<^{\text{C}_6\text{H}_4}_{\text{C}_6\text{H}_4}\!\!>\!\!\text{C·OBz,}$$
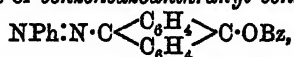
m. p. 230—231°, dark red crystals with a metallic lustre, which is prepared by treating benzeneazoanthranol in acetone with aqueous sodium hydroxide and benzoyl chloride in the cold; by prolonged boiling with alcoholic hydrochloric acid, it yields benzoic acid, anthraquinone, and phenylhydrazine. On the contrary, *anthraquinonebenzoylphenylhydrazone*, $\text{NPhBz·N:C}\!\!<^{\text{C}_6\text{H}_4}_{\text{C}_6\text{H}_4}\!\!>\!\!\text{CO}$, m. p. 172—173°, orange-yellow prisms, prepared by heating 9 : 9-dibromoanthrone, alcoholic benzoylphenylhydrazine and sodium carbonate, develops a yellow coloration with concentrated sulphuric acid, does not form additive compounds with metallic chlorides, is only slowly attacked by alcoholic bromine, and is rapidly hydrolysed by boiling dilute acetic acid. It cannot be transformed into benzeneazoanthranyl benzoate by ether and powdered potassium hydroxide.

Anthraquinonephenylmethylhydrazone, $\text{NPhMe·N:C}\!\!<^{\text{C}_6\text{H}_4}_{\text{C}_6\text{H}_4}\!\!>\!\!\text{CO}$,

m. p. 147—148°, red prisms with metallic lustre, is obtained by heating 9 : 9-dibromoanthrone with alcoholic *as*-phenylmethylhydrazine or by treating benzeneazoanthranol in aqueous acetone with sodium hydroxide and methyl sulphate. It is not affected by alcoholic potassium hydroxide, but is hydrolysed to anthraquinone and *as*-phenylmethylhydrazine by boiling dilute acetic acid or alcoholic hydrochloric acid. It is thus seen that the acylation of benzeneazoanthranol in alkaline solution is a process of direct substitution (an *O*-ester being formed), whilst the alkylation is a case of addition followed by elimination (an *N*-ether being formed).

At the present time aliphatic hydroxyazo-compounds, such as phenylazoacetylacetone, are generally regarded as hydrazones, for example, NHPh·N:C(COMe)_2, because they yield *N*-esters [NBzPh·N:C(COMe)_2] by acylation. The evidence is by no means conclusive, however, because the hydroxyazo-compound can yield the *N*-ester as follows :

$$\text{ONa·CMe:C(N:NPh)·COMe} \longrightarrow \overset{\text{NaO}}{\underset{\text{Cl}}{}}\!\!>\!\!\text{CMe·C(:N·NBzPh)·COMe}$$

$\longrightarrow$ NBzPh·N:C(COMe)$_2$. The colour, solubility in aqueous alkalis,
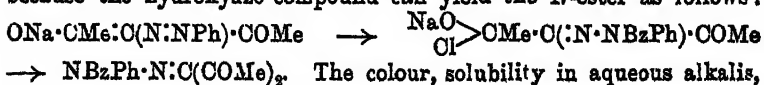
and reactivity with alcoholic bromine are all in harmony with the formulation of aliphatic hydroxyazo-compounds as hydroxyazo-compounds.

Anthraquinoneoxime is obtained by treating 9 : 9-dibromoanthrone with alcoholic hydroxylamine and dry sodium carbonate. The same substance is at once precipitated when its alkaline solution is acidified with sulphuric acid at 0°; nitrosoanthranol is not isolated.   C. S.

Action of Acids on Proteins. D. CALUGĂREANU (*Bull. Acad. Sci. Roumaine*, 1912/13, **1**, 40—42).—With the object of deciding whether the products of the action of acids on proteins are chemical compounds which are hydrolytically dissociated in aqueous solution, or are simply adsorption products, the author has studied the electrical conductivity of a number of acids (hydrochloric, sulphuric, chromic, acetic, citric, lactic, trichloroacetic, and picric) at different dilutions in aqueous solution, on the one hand, and in aqueous solution in the presence of various proteins (serum-albumen, serum-globulin, and gelatin) on the other, the experimental conditions being so chosen that the concentration of the protein remains constant, the concentration of acid alone varying.

Since the curves obtained are closely similar to that given by a solution of glycine under similar conditions, the author is led to the conclusion that the form of the curve is largely due to the hydrolytic dissociation of the product of the action of acids on the protein. He does not consider, however, that the phenomenon of adsorption is completely excluded.   H. W.

The Relations of the Phenols and their Derivatives to Proteins. Mechanism of Disinfection. II. Effects of Various Factors on the Germicidal and Protein-precipitating Powers of the Phenols. EVELYN A. COOPER (*Biochem. J.*, 1913, **7**, 175—185. Compare A., 1912, ii, 1199).—The introduction of hydroxyl groups decreases, and of nitro- or methyl groups, increases, the bactericidal and protein-precipitating powers of phenol. The monohydric phenols are superior to the alcohols in both directions. Sodium chloride increases both properties through increasing the solubility of phenols in proteins; alcohol behaves in the opposite way. Solutions of phenol in fat possess no such activities. Small amounts of alkali inhibit the power to precipitate proteins, without affecting the germicidal power; the explanation of this is not apparent. The precipitating action of phenol is increased by the addition of acids. The absorption of phenols by bacteria is the initial stage in disinfection; the germicidal action is not due to a union of the phenols with the bacterial protoplasm (as with formaldehyde), but to a de-emulsifying action upon the colloidal suspension of some constituent protein or proteins essential for the vitality of the organisms.

W. D. H.

The Relations of the Phenols and their Derivatives to Proteins. Mechanism of Disinfection. III. The Chemical Action of *p*-Benzoquinone on Proteins. EVELYN A. COOPER (*Biochem. J.*, 1913, **7**, 186—196).—*p*-Benzoquinone gives a red colour

with various proteins and amino-acids (confirmatory of Würster and Raciborski); the proteins can be isolated in a coloured state from the solutions, but could not be decolorised. Their solubilities and other properties are changed, hence they had been chemically altered. *p*-Benzoquinone in absolute alcohol does not produce the colour; and treatment of the proteins with formaldehyde inhibits the reaction, except in the case of gelatin, aniline, and ammonia. The effect of formaldehyde indicates that proteins, proteoses, and amino-acids react with *p*-benzoquinone through their amino- or imino-groups. No colour reaction was obtained with *p*-benzoquinonedioxime, which shows probably that the reacting groups of the proteins condense with the ketonic groups of the quinone. The effect of the latter therefore resembles that of formaldehyde. Acetone differs from *p*-benzoquinone by acting as a protein precipitant. The germicidal power of *p*-benzoquinone is due to its chemical action on some constituent protein or proteins of the bacteria. W. D. H.

Nitro-derivatives of the Proteins. ALBRECHT KOSSEL and FRANZ WEISS (*Zeitsch. physiol. Chem.*, 1913, **84**, 1—10).—The arginine group in the molecule of the higher proteins is as accessible to nitration by means of a mixture of concentrated nitric and sulphuric acids as that in the protamines.

Nitroclupeine, like nitroarginine, when digested at 38° with normal sodium hydroxide solution loses carbon dioxide, ammonia, and nitrous oxide, a derivative of ornithine being formed. The amount of gas formed confirms this interpretation of the change, and the method is applicable to the determination of the nitro-group in nitroguanidine and of the nitroamino-groups in nitrated proteins.

In the case of edestin it is shown that in addition to the guanidine complex of the arginine constituent a further guanidine complex is present in the molecule, which forms a nitroamine. This is in agreement with Otori's (A., 1904, i, 1067) suggestion of such a second guanidine complex in ψ-mucin, casein, and gelatin. E. F. A.

Action of Arsenious Acid, Arsenic Acid, and Phosphoric Acid on Albumin. CORRADO BONGIOVANNI (*Gazzetta*, 1913, **43**, i, 161—163).—From measurements of the conductivity of solutions of albumin and of the above acids separately, and of the binary mixtures of the acids with albumin, the author finds no evidence that combination with the albumin occurs. The diminution of conductivity which takes place on mixing is to be ascribed to a lessening of the mobility of the ions by the colloidal substance. R. V. S.

Acid Decomposition Products of Hæmin. OSKAR PILOTY and EDMUND DORMANN (*Ber.*, 1913, **46**, 1002—1008).—The acid decomposition products of hæmin obtained on reduction with hydrogen iodide and acetic acid contain four components: phonopyrrolecarboxylic acid, xanthopyrrolecarboxylic acid, *iso*phonopyrrolecarboxylic acid, and an acid so far only obtained as a syrup.

In view of the possibility that xanthopyrrolecarboxylic acid, $C_{10}H_{15}O_2N$, might be *iso*phonopyrrolecarboxylic acid, $C_9H_{13}O_2N$,

contaminated with the product of the action of ethyl alcohol on its picrate, it has been further investigated and its individuality established.

The picrate of phonopyrrolecarboxylic acid when heated in ethyl or methyl alcoholic solution in presence of free picric acid is rapidly and completely esterified at the carboxyl group. The free methyl ester crystallises in long, flat, colourless needles, m. p. 59°; its picrate has m p. 122°. The corresponding *ethyl* ester forms six-sided, colourless plates, m. p. 134°; its *picrate* crystallises in pale yellow, flat, prismatic needles of rhombic habit, m. p. 93°.

The acid mixture yields a fourth crystalline acid, $C_{10}H_{15}O_2N$, *phonopyrrolecarboxylic acid*-d, which crystallises in colourless needles pointed at either end. The *picrate* separates in characteristic yellow crystals, m. p. 132°. The new acid is perhaps identical with compounds described by H. Fischer (A., 1912, i, 384, 901), and obtained by the action of sodium methoxide on pyrrole derivatives.   E. F. A.

Sulphuric Acid Hæmatoporphyrin. ANT. HAMSIK (*Zeitsch. physiol. Chem.*, 1913, 84, 60—66).—Hæmatoporphyrin, prepared from hæmin by means of concentrated sulphuric acid, was obtained as an amorphous, dark blue powder. By solution in acetic acid containing 10% of water, the addition of concentrated hydrochloric acid, and enough dilute acid to make the amount of water 40%, the pigment was obtained partly crystalline in dark green needles or long rods, usually aggregated in stellate or bunched clusters, and partly crystalline in red aggregates of varying size, or in indefinite green masses.

Crystals were also obtained by dissolving the original product in acetone and hydrochloric acid.   E. F. A.

The Kinetics of Invertin Action. LEONOR MICHAELIS and (Miss) MAUD L. MENTEN (*Biochem. Zeitsch.*, 1913, 49, 333—369).—The authors, whilst accepting generally Victor Henri's generalisations as to the method of the ferment action, call attention to two defects in his experimental method. They show that the hydrogen-ion concentration of the solutions has not been taken into account, and that the multirotation of sugar has been neglected. They remedy the first defect by working in an acetate mixture, prepared according to Sörensen, which gives the optimal conditions of action, and they remedy the second defect by reading the polarisations after the sugar mixture has been allowed to remain with sodium hydroxide solution, which inhibits the action of the ferment. Like Henri, therefore, they use the polarimetric method for investigating the change. They assume that the invertin enters into combination with sucrose to form a labile compound, which decomposes according to the scheme : 1 mol. sucrose–invertin compound $\longrightarrow$ 1 mol. dextrose + 1 mol. lævulose + 1 mol. invertin. It is only through the intermediation of the sucrose–invertin compound that inversion takes place. The invertin can also combine with the scission products to form compounds, but as these are not labile, the only effect of their formation is to diminish the amount of ferment available for combination with the sucrose, and thus to inhibit the inversion. The present communication deals chiefly with the

methods for the determination of the dissociation constants of the various invertin–sugar compounds. For sucrose, the following equation is evolved : $v = C\Phi.[S]/([S]+k)$, where v is the initial reaction velocity, C is a constant depending on the arbitrarily chosen units employed for measuring change (in this case the rotation changes), S is the concentration of the sugar. k the dissociation constant, and Φ the concentration of the ferment. If Φ is kept constant and S is altered, $v/C\Phi$ can be replaced by V, and the equation becomes $V=[S]/([S]+k)$, which is identical in form with the residuary dissociation curve of an acid. The methods are given (graphic and others) for determining k, which for the sucrose–invertin compound was found to be 0·0167. By measuring the inhibition of inversion produced by various carbohydrates, the dissociation constant of the compounds of invertin with other sugars was ascertained. For this purpose the equation : $k^1 = Fk/\{(S+k)(v_0/v_1 - 1)\}$, was evolved. where k^1 is the constant in question, F is the amount of inhibitory sugar, v_0 and v_1 the initial rates of inversion in the presence and absence of inhibitory sugars (such as lævulose), and the other symbols have the meanings already described. It was found that mannitol and glycerol, as well as carbohydrates, had a power of combining with invertin, but that the affinity for these of the ferment, as determined by the dissociation constants, was less than that for sucrose. Lactose had practically no combining power, and therefore does not appreciably inhibit sugar inversion. The decomposition of the sucrose–invertin compound was found to be a unimolecular reaction. S. B. S.

The Dialysis of Maltase. LADISLAS KOPACZEWSKI (*Compt. rend.*, 1913, **156**, 918—921).—A sample of maltase (taka-diastase) was submitted, first to ordinary dialysis, and then to Dhéré's process of electrical dialysis (compare A., 1910, ii, 515). Ordinary dialysis causes the hydrolysing power of the maltase to increase very considerably to a maximum (200% of original power), after which it diminishes slightly to 180%. Prolonged dialysis produces no further change. Electrical dialysis at this stage removes more of the electrolytes present, and produces a slight further diminution in the diastatic power. The maltase travels in the electrical field towards the negative pole ; thus purified, the maltase has a feebly acid reaction to helianthin, and conductivity measurements give $K = 3\cdot8 \times 10^{-6}$.
W. G.

Action of Ammonia Gas on Diastase. III. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **84**, 161—188. Compare A., 1912, i, 113).—When dry ammonia gas is passed over diastase preparations a small quantity is absorbed. In addition to ammonium salt formation and physical adsorption, ammonia is taken up and an equivalent of water liberated in two ways. In one instance an atomic group is formed, which combines both with acids and with formaldehyde ; in another, the new group has neither of these properties. Such changes are assumed to indicate the replacement of an alcoholic hydroxyl by an amino-group and the interaction of an aldehyde group with ammonia.

The enzymic activity of the diastase is increased rather than hindered by the action of the ammonia. It is assumed that diastatic activity is not connected with the presence of a free aldehyde group or of an alcoholic hydroxyl.   E. F. A.

The **Reversibility of Ferment Actions**: Emulsin and β Methyl Glucoside. EMILE BOURQUELOT and ÉMILE VERDON (*Compt. rend.*, 1913, **156**, 957—959).—Experiments on β-methyl glucoside and emulsin confirm in every respect the results previously obtained with β-ethyl glucoside (compare Bourquelot and Bridel, A., 1912, i, 928 ; this vol., i, 212 ; Bourquelot and Coirre, this vol., i, 410).   W. G.

Action of High Temperatures on the Dried Nucleases of Vegetable Origin. E. C. TEODORESCO (*Compt. rend*, 1913, **156**, 1081—1084. Compare A., 1912, i, 1042).—A study of the effect of heat on the enzymatic properties of dried nucleases from four different sources of vegetable origin. The dried nucleases of the plants studied only lose their activity towards sodium nucleate after heating for thirty minutes at the following moderately high temperatures. The nuclease from *Evernia prunastri* becomes inactive at 145°, that from *Lycoperdon gemmatum* between 141° and 156°, that from brewer's yeast at 153°, and that from *Sticta pulmonacea* at 162°.   W. G.

Preparation of a Nitro-3-aminophenyl-1-arsinic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 256343).— Two isomeric nitroaminophenylarsinic acids are known, and the third isomeride has now been prepared as follows :

Carboethoxy-m-arsanilic acid, m. p. 180° (decomp.), is obtained by treating an aqueous solution of 3-aminophenylarsinic acid with ethyl chloro-formate ; this, when dissolved in fuming sulphuric acid at 0° and treated with nitric acid (26%), furnishes the corresponding *nitro*-compound (a yellow, crystalline powder), which, on hydrolysis at 70—80° with concentrated sulphuric acid, gives rise to 2-*nitro-3 amino-phenylarsinic acid*, orange-yellow needles.

2 : 3-*Diaminophenylarsinic acid*, obtained by reducing the preceding compound with sodium hyposulphite at the ordinary temperature, forms glistening leaflets, m. p. 205—208° ; it furnishes an *azoimide* on treatment with nitrous acid.

2-*Nitro-3-hydroxyphenylarsinic acid* is obtained by the action of concentrated potassium hydroxide on 2-nitro-3-aminophenylarsinic acid, and this on reduction with sodium hyposulphite gives rise to 2 : 2'-*diamino-3 : 3'-dihydroxyarsenobenzene*.   F. M. G. M.

Physiological Chemistry.

Oxidising and Reducing Enzymes and their Rôle in the Process of Respiration. ALEXIS BACH (*Arch. Sci. phys. nat*, 1913, **35**, 240—262).—A summary of the present knowledge of the subject. Emphasis is laid on the following conclusions. (1) In order to utilise the oxygen of the air to effect oxidation, the cell produces an enzyme (an oxygenase), a substance which is readily oxidised, fixing molecular oxygen to form a peroxide. (2) A second enzyme (the peroxydase) accelerates the oxidising action of the peroxides, acting on them in the same way as ferrous sulphate does towards hydrogen peroxide. (3) The peroxides are readily transformed by hydrolysis into hydrogen peroxide, which is also formed as a primary product during hydrolytic oxidation. Owing to its rapid rate of diffusion, this accumulation of hydrogen peroxide might damage the cell protoplasm. To guard against this, the cell produces an enzyme-catalase, which rapidly decomposes hydrogen peroxide into water and inert oxygen. Catalase thus acts as a regulator of the respiratory process. (4) To effect hydrolytic oxidation, an enzyme, perhydridase, is present, which accelerates both oxidation and reduction just as do the metals of the platinum group. The reductase consists of the enzyme, water, and an oxidisable substance which fixes the oxygen derived from the water, leaving the hydrogen free to effect reduction. E. F. A.

Mechanism of Stimulation by Lack of Oxygen. H. S. GASSER and ARTHUR S. LOEVENHART (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxx—xxxi; *J. Biol. Chem.*, **14**).—Lack of oxygen decreases the oxidation, and so stimulates the cells of the respiratory, cardio-inhibitory, and vaso-motor centres. Decrease in oxidation stimulates per se, and not by the accumulation of katabolic products. W. D. H.

The Relationship between the Sugar Content of Erythrocytes and Glycolysis. ADAM LOEB (*Biochem. Zeitsch.*, 1913, **49**, 413—425).—Observations of previous observers are confirmed, according to which the red blood corpuscles of different species possess different contents of sugar, which are characteristic of each species. In the case of man, the corpuscles contain about the same percentage of sugar as the serum; in the dog they contain less, and in the case of sheep and pig, the corpuscles only contain very small amounts of sugar. The corpuscles of ox occupy an intermediary place as regards the sugar content. The larger the sugar content of corpuscles, the greater the amount of glycolysis they produce on incubation. The conclusion is drawn that those corpuscles produce glycolysis most readily which are the most readily permeable by sugar. Glycolysis of added sugar is therefore not wholly dependent on the presence of white corpuscles. S. B. S.

Oxycholesterol. E. SCHREIBER and LENÁRD (*Biochem. Zeitsch.*, 1913, **49**, 458—465).—This substance pre-exists as such in the blood. It is also found in the brain, lungs, heart, intestine, spleen, kidneys, muscles, sometimes in the pancreas. It is, however, not present in the liver. The failure to find the substance in this organ is shown not to be due to imperfect technique. Oxycholesterol is absent from the blood in diabetic coma. Preliminary experiments are described which are directed towards ascertaining the action of the liver towards oxycholesterol.   S. B. S.

The Nature of the Destruction of Hæmoglobin during the Autolysis of Organs. SOICHIRO MIURA (*Biochem. Zeitsch*, 1913, **49**, 137—143).—The disappearance of the blood pigment from autolysing mixtures, as observed by Hess and Saxl, is confirmed. This is not due to an enzyme in the mixture, but is a coagulative process, which takes place rapidly in the presence of chloroform, which is used as an antiseptic; the blood colour disappears from solution, in fact, when a solution is incubated with chloroform without the presence of any organ. The hæmatin component remains unchanged in quantity during the process of incubation. When organs are present, the coagulum is carried down with the solids.   S. B. S.

The Action of Leucocytes on Some Hexoses and Pentoses. III. Mechanism of Lactic Acid Formation from Carbohydrates. PHŒBUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem*, 1913, **14**, 149—154).—Leucocytes transform dextrose into *d*-lactic acid, but cleavage does not proceed further. There must be many intermediate stages in this change. Embden's view that glyceraldehyde is one is not confirmed. Moreover, regardless of the nature of the hexose (mannose, lævulose, galactose, dextrose), the lactic acid is invariably of the *d*-form. Whether pyruvaldehyde is the phase immediately preceding the formation of lactic acid remains to be established. Tissues preserved under aseptic conditions act similarly. Dissociation of pentoses by leucocytes does not occur.   W. D. H.

The Behaviour of Calcium in the Serum. PETER RONA and DENGO TAKAHASHI (*Biochem. Zeitsch.*, 1913, **49**, 370—380).—The dependence of the solubility of calcium on the hydrogen and hydrogen carbonate concentration was investigated. The values, according to the laws of mass action of $k_1 = [Ca^{..}][HCO_3]_2/[H_2CO_3]$ and $k_2 = [Ca^{..}][HCO'_3]/[H]$, were determined. The experimental method of determining these constants is given in detail, and the values $k_1 = 116·10^{-6}$ and $k_2 = 350$ were found. Serum was submitted to dialysis against an outer fluid of definite volume of known hydrogen carbonate concentration, and the composition of the inner and outer fluids was ascertained when equilibrium had been established. From the data thus obtained, the conclusion is drawn that the calcium hydrogen carbonate is in free diffusible form, but forms metastable supersaturated solutions. By the method of com-

pensation dialysis, against known phosphate mixtures, results were obtained indicating that the phosphate is also freely diffusible. The non-diffusible calcium appears therefore to exist in the form of calcium protein compounds. S. B. S.

Mode of Action of the Anti-coagulating Substance of the Plasma of Propeptone. HENRI STASSANO (*Compt. rend.*, 1913, **156**, 912—915).—A continuation of previous work (compare this vol., i, 418) on the coagulation of the plasma of propeptone. On diluting samples of the plasma with equal volumes of solutions of different chlorides of equivalent strength, the period of time, prior to coagulation, increases with rise in molecular weight of the chloride. Diminution of the saline concentration by dialysis, or marked increase of it by addition of sodium chloride, produces coagulation. Addition of a strongly negative colloid hastens coagulation. The following conclusions are drawn: (1) In the plasma of propeptone the coagulation, in vitro, takes place in two stages: activation of the fibrin-ferment, followed by its action on the fibrinogen. There is also a third stage, commencing when the colloidal stability of the fibrinogen is brought about, which consists in the appearance of granules in the uniform gel, this phenomenon being very fugitive and only visible under the ultramicroscope in the case of blood. (2) The anti-coagulating substance of the propeptone plasma forms a complex with the fibrinogen, hindering its precipitation and giving rise to a coagulum, without the intervention of one of the above-mentioned methods. W. G.

Digestion in the Chick. T. P. SHAW (*Amer. J. Physiol.*, 1913, **31**, 439—446).—Extracts of the glandular structures of the floor of the mouth in the chick contain an amylolytic enzyme active in an alkaline medium. This was found in extracts made an hour after hatching. The crop secretes no enzymes, but simply retains the food whilst salivary digestion goes on. By the second day, the gastric juice secreted contains proteolytic and milk-curdling enzymes which are active in an acid medium. The functions of the pancreas are imperfectly developed before the seventh day after hatching; the pancreatic juice then contains the usual three enzymes. The liver contains glycogen on the twentieth day of incubation; it becomes glycogen-free twenty-four hours after hatching if no food is given. It is found in the liver on the second day after the administration of starchy food. Lactose is not a glycogen-former in chicks, but acts as an irritant to the gastric and intestinal mucous membrane. W. D. H.

The Dependence of Lipase Action on the Concentration of the Hydrogen Ion. HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1913, **49**, 249—277).—The lipoclastic action was investigated by the stalagmometric method with the employment of tributyrin as substrate. The optimal action of the duodenal lipase of sucklings (withdrawn by means of a tube) was at $[H^{\cdot}] = 3.2 \times 10^{-9}$ or $p_H = 8.5$. A series of experiments was carried out with the same amount of

ferment in solutions of different hydrogen ion concentrations, and the course of lipolysis investigated. It was assumed that, except under optimal conditions, a fraction only of the ferment was active, and a method is given of calculating this fraction. If this amount is plotted graphically as a function of the hydrogen ion concentration, a curve is obtained which is identical with the dissociation curve of a weak acid, and is of the same order of magnitude as a curve deduced in a similar manner for trypsin. The conclusion is drawn that the lipase, like trypsin, is an amphoteric electrolyte with the acid dissociation constant $k_a = 1 \cdot 0 \times 10^{-7}$. The lipolytic activity is proportional to the amount of ferment ion present. The lipase of the stomach has a broad optimal zone with $[\dot{H}]$ between 10^{-5} and 10^{-4}. The curve obtained for this ferment is similar to the invertin curve, and is that of the residuary dissociation curve of an ampholyte with the constant $k_a = 4 \cdot 5 \times 10^{-7}$. The active principle of the stomach lipase is bound to the dissociation residue, and the optimal activity corresponds with the isoelectric point of the ampholyte, the basic dissociation constant of which is about 10^{-12}. There is therefore a difference between the gastric and duodenal lipases, which can be distinguished from one another by ascertaining the optimal $[\dot{H}]$ concentration for their action. There is no evidence in the case of sucklings of regurgitation from duodenum. The lipase of human milk is apparently a pancreatic lipase.

S. B. S.

Method of Investigating Metabolism in Rabbits, Milk being the Only Food. ERNST LAQUEUR (*Zeitsch. physiol Chem.*, 1913, **84**, 109—116) —A specially constructed cage for metabolism experiments on rabbits is described. For prolonged periods milk was the only nutriment given. The advantages of milk are that its nitrogen is easily estimated, the urine does not readily decompose, and its secretion is regular. The absorption of milk is rapid, and 95% of it is utilised as compared with 65—70% of oats and cabbage.

W. D. H.

Amino-acids and Sugar for Rectal Feeding HUBERT W. BYWATERS and A. RENDLE SHORT (*Arch. expt. Path Pharm.*, 1913, **71**, 426—445).—The older observations on the nutritive value of enemata are untrustworthy. Not a trace of milk or egg (peptonised for twenty to thirty minutes) is absorbed. Amino-acids, however, are absorbed, and lead to an increase in urinary nitrogen; the ammonia is low in the urine, hence the absorption of putrefaction products is absent. Dextrose is better absorbed than lactose; fat is badly absorbed. The best enema for rectal feeding is milk which has been subjected to pancreatic digestion for twenty-four hours plus 5% of dextrose.

W. D. H.

The Functions of the Liver in the Metabolism of Fats. I. HENRY S. RAPER (*J. Biol. Chem.*, 1913, **14**, 117—134) —Cocoanut oil given to cats or dogs by the mouth can be detected in the liver in five to six hours. The amount present does not exceed 6% of

that absorbed. If cocoanut oil soap plus glycerol and bile are injected into the intestine of anæsthetised cats, about 30% of the absorbed fatty acid is found in the liver. If an emulsion of the oil is given intravenously, 25—60% is found in the liver. During absorption the fat in the chyle contains fatty acids with an average higher molecular weight than in the oil. The lower acids are therefore partly absorbed as sodium salts. The volatile acids from the liver absorb more iodine than those from normal livers. The increase is not great, but it probably indicates that saturated fatty acids containing 10, 12, or 14 carbon atoms may become unsaturated in the liver.   W. D. H.

The Influence of Urea Administered by the Mouth on the Nitrogenous Metabolism of Pigs. EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch physiol. Chem*, 1913, **84**, 218—222).—No evidence was found to support the view that urea in the food acts as a protein sparer. In reference to gelatin, attention is drawn to the fact that various commercial specimens yield as much as 1% of tyrosine, and may even yield tryptophan. It is evident that no certain conclusions as to the nutritive value of gelatin can be drawn from experiments with such variable material.   W. D. H.

Nitrogen Retention after Feeding on Urea. Reply to Abderhalden and Lampé EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, **84**, 234—238).—Polemical. The author maintains the correctness of his earlier conclusions.   W. D. H.

Influence of Caffeine on Creatine and Creatinine Metabolism WILLIAM SALANT and J. B. RIEGER (*Proc. Amer. Soc. Biol. Chem*, 1912-13, xxxv; *J. Biol. Chem*, **14**).—Caffeine causes a moderate increase in the urinary creatine in fed rabbits, but a large increase during inanition; in some experiments, however, neither creatine nor creatinine were affected. Experiments on dogs gave negative results.   W. D. H.

Metabolism of Nitrogenous Sugar Derivatives. JAMES ARTHUR HEWITT (*Biochem. J.*, 1913. **7**, 207—210). — Dextrose-*p*-phenetidide given by the mouth or by injection is not toxic in amounts up to 4 grams per kilo. of body weight. It produces no effect on nitrogenous metabolism, but a reducing substance appears in the urine. Some escapes oxidation in the body; *p*-phenetidine in amounts of 0·1 gram per kilo. of body weight is highly toxic.
                                        W. D. H.

The Action of Carbon Dioxide on Metabolism. Autolysis and Metabolism. VI. ERNST LAQUEUR (*Zeitsch. physiol. Chem.*, 1913, **84**, 117—160).—The nitrogenous metabolism was investigated on rabbits during a milk diet and inanition. Carbon dioxide slows and deepens the breathing; little or no narcotic action was observed. Nitrogenous metabolism was unaffected by a carbon dioxide percentage up to 7%. At 10% the output of nitrogen was increased,

at 13% very markedly so. In half the experiments this was accompanied by retention of water. The high tension of the gas is regarded as the cause of the increased decomposition of tissue-protein, possibly because the activity of autolytic enzymes is heightened.   W. D. H.

Synthetic Powers of Animal Cells. The Action of Sodium Nitrate on Nitrogenous Metabolism. EMIL ABDERHALDEN and PAUL HIRSOH (*Zeitsch. physiol. Chem.*, 1913, 84, 189—200).—Nitrogen given in the form of sodium nitrate is excreted quantitatively in the urine; it takes no direct part in protein metabolism. In two cases, however, there was retention of nitrogen, which did not correspond with the nitrogen given in the form of sodium nitrate. This is important as showing that nitrogen retention may be the result of the administration of nitrogenous materials which do not participate in metabolism.   W. D. H.

Utilisation of Ammonia Nitrogen in Protein Metabolism. ALONZO E. TAYLOR and A. L. RINGER (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxvi—xxvii; *J. Biol. Chem.*, 14).—The findings of Grafe and of Abderhalden are confirmed, that starving and diabetic animals may retain a considerable part of the nitrogen ingested as ammonium carbonate.   W. D. H.

Nitrogenous Assimilation on Feeding on Small Amounts of Protein and Large Amounts of Ammonium Salts and Urea. EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, 84, 69—96).— The favourable action of ammonium salts and urea given by the mouth in pigs in causing retention of nitrogen is supported by further experimental data. By themselves, however, they do not maintain nitrogenous equilibrium over prolonged periods, but in combination with a small amount of protein they do. In other words, they have a protein sparing action. Whether their nitrogen is converted into protein or not is discussed, but no definite conclusion reached. The paper concludes with polemics against Abderhalden and Lampé, whose experiments are held to support and not disprove the author's contentions.   W. D. H.

The Location of Protein Synthesis and the Production of Nitrogenous Equilibrium with Minimal Amounts of Proteins of Varying Decomposibilities. HANS STECK (*Biochem. Zeitsch*, 1913, 49, 195—224).—It has been assumed that the chief seat of synthesis of proteins is in the mucous membrane of the small intestine. If this is the case, those proteins which most readily undergo enzymatic hydrolysis into their constituent amino-acids will be the most efficient in maintaining nitrogenous equilibrium (that is, will maintain equilibrium when ingested in the smallest quantity), provided that the energy needs of the organism are sufficiently satisfied by the caloric value of the fats and carbohydrates. The reason for this assumption is that the majority of the amino-acids necessary for protein synthesis will be present at

the same time in the intestine in those proteins which are readily hydrolysed. The method of experiment adopted by the author was to place himself on a diet of sufficient caloric value and nearly free from nitrogen, and then to estimate the nitrogen loss. On this diet various proteins were superimposed, and the quantity was ascertained in each case, which is just necessary to restore the nitrogenous equilibrium. It was found that after three days of protein-free diet, the superimposition of small quantities of beef, egg-albumin, and caseinogen could restore equilibrium, but the amounts bore no relationship to their decomposability by proteoclastic ferments. The conclusion is drawn therefore, that protein synthesis takes place in parts of the organism other than the small intestine. From the amounts of nitrogen secreted in the after period, it appears that the ingestion of these proteins results in protein synthesis in the organism. Hæmoglobin, when ingested in small quantities, was inefficient in maintaining nitrogenous equilibrium. S. B. S.

The Influence of the Plane of the Protein Intake on Nitrogen Retention in the Pig. ELMER V. McCOLLUM (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxxiii—xxxiv; *J. Biol. Chem.*, 14). —The retention of nitrogen at all levels, except 7·5 times the endogenous level, was in close agreement, whether the proteins given were derived from wheat, oats, or maize. At five times this level, 10% of the ingested nitrogen was retained; at 7·5, 12—17%; at 10, 15, and 20, the retention was 21—24%. W. D. H.

Metabolic End-Products of the Lipoid Nitrogen of Egg-yolk. ELMER V. McCOLLUM and H. STEENBOCK (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xliv—xlv; *J. Biol. Chem.*, 14).—A pig was fed for a week on 220 grams of dry egg-yolk and 35 grams of starch per diem. The nitrogen intake was 11·65 grams daily; of this, 0·65 gram was lipoid nitrogen. The urinary nitrogen varied from 5 to 6 grams; of this 30 to 40% was in the form of ammonia, and only 35—45% as urea. The urine contained 0·3 gram of nitrogen as substituted amines. The demethylation of substituted amines is evidently not readily accomplished in the pig's body. W. D. H.

The Biological Value of a-Nucleic Acid. G. ALLESANDRO BROSSA (*Chem. Zentr.*, 1912, ii, 2123; from *Arch. Anat. Physiol.* (*Physiol. Abt.*), 1912, 191—196).—A dog and two hens were reduced to a nitrogen-free diet balanced by increased amounts of carbohydrates and fats, and then supplied with a-nucleic acid. Estimation of nitrogen in the excreted substances showed that 60—80% of the nucleic acid, a compound which is far removed from the proteins, had been absorbed. J. C. W.

Resorption of Bromide from the Intestine. STEFAN VON BOGDÁNDY (*Zeitsch. physiol. Chem.*, 1913, 84, 15—17).—To study the resorption of bromide from the intestine, the blood stream was limited to the intestine, heart, and lungs, and the haloids in it determined before and after injection of sodium bromide. The

bromide is shown to aggregate in the blood in a very short interval; part of the sodium chloride of the blood is replaced by bromide.

<div align="right">E. F. A.</div>

The Fate of Protein Cleavage Products in the Intestine.

EMIL ABDERHALDEN, ARNO ED. LAMPÉ, and EFIM S. LONDON (*Zeitsch. physiol. Chem.*, 1913, **84**, 213—217).—Accepting the view that in absorption protein cleavage products enter the blood stream as amino-acids and ammonia, there still remains the possibility that the lacteals may be a channel for protein absorption. In two series of experiments on dogs, the lymph during digestion of meat was found to contain more nitrogen but less amino-acid than during hunger; the amount of ammonia was but little altered. Further work in this direction is promised.

<div align="right">W. D. H.</div>

The Absorption of Magnesium Sulphate Solutions in the Small Intestine, and the Mode of Action of Saline Purgatives.

RUDOLF COBET (*Pflüger's Archiv*, 1913, **150**, 325—360).—The relative importance of physical and physiological factors in the causation of purgation by salines is discussed. Magnesium sulphate causes a great increase of secretion in the intestines; the sodium chloride of the intestinal juice poured out is re-absorbed in the lower reaches of the gut, but the fluid portion is not; the sulphate itself is badly absorbed.

<div align="right">W. D. H.</div>

Intestinal Obstruction. A Toxic Substance in the Intestinal Mucosa.

GEORGE H. WHIPPLE (*Proc. Amer. Soc. Biol. Chem.;* 1912–13, xxxii—xxxiii; *J. Biol. Chem.*, **14**).—Closed loops of the small intestine yield what normal mucosa does not yield, a toxic substance which causes low blood-pressure, vomiting, diarrhœa, collapse, and death. If the mucosa is first destroyed by sodium fluoride, no toxic substance is formed.

<div align="right">W. D. H.</div>

The Influence of Function on the Lime Requirements of Animals.

H. STEENBOCK and EDWIN B. HART (*J. Biol. Chem.*, 1913, **14**, 59—73).—In the non-pregnant animal a daily intake of 0·3 gram of CaO in the pig, and 0·4 in the goat per 100 lbs. of body-weight covers metabolic losses; but mammary activity is a severe drain on the skeletal lime, and the allowance in the food should be three or, better, six times greater, for increase of food entails large losses of lime in the intestine.

<div align="right">W. D. H.</div>

The Effect of a High Magnesium Intake on Calcium Retention in Swine.

EDWIN B. HART and H. STEENBOCK (*J. Biol. Chem*, 1913, **14**, 75—80).—Bran is not a good bone producer, on account of its low lime content. Magnesium salts added to a pig's ration increase the urinary calcium, but this is counteracted by di-potassium hydrogen phosphate. The inter-relations existing between the mineral elements are important factors in nutrition.

<div align="right">W. D. H.</div>

The Behaviour of Plasteins in the Animal Body. ERICH VON KNAFFL-LENZ and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1913, **71**, 407—425).—Plasteins act as antigens, but the immune material generated is not specific. The specificity of the original proteins is thus destroyed during digestion. It further makes no difference what variety of pepsin is employed in their formation. Plasteins do not produce the phenomena of anaphylaxis.

W. D. H.

The Influence of the Composition and Amount of the Mineral Content of the Ration on Growth. ELMER V. MCCOLLUM and MARGUERITE DAVIS (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xl; *J. Biol. Chem.*, **14**).—Young rats do not grow when fed on wheat kernel only, but the addition of salts so as to make the ration like that of milk or egg-yolk produced normal growth.

W. D. H.

The Chemical Changes Occurring in Meats during Drying in a Vacuum. L. H. DAVIS and A. D. EMMETT (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xlii; *J. Biol. Chem.*, **14**).—Calculating the data for fresh and desiccated meats to the dry basis, using the two values for dry substance (the vacuum and the oven-heated), the results agree closely for the various constituents, the differences being greatest in the fat, as was to be expected. W. D. H.

The Presence of Choline or Allied Bases in the Saliva of the Horse. JULES HOUDAS (*Compt. rend.*, 1913, **156**, 824—826) — Schulze and Trier (A., 1912, ii, 1203) having demonstrated the presence of choline and allied bases in all plants, the author has examined the saliva of horses for the presence of these substances therein, using Bouchardat's reagent to recognise them. Specimens of saliva were obtained from horses under varying conditions and at different times after feeding and with varying diet, and in all cases either choline or bases of the same group were found to be present. W G.

The Central Nervous System under Normal and Pathological Conditions. V. Biochemical Studies on Brain Swelling : (*a*) Acute Brain Swelling and the Colloidal Theory of Œdema. GIACOMO PIGHINI, PIETRO BARBIERI, and DOMENICO CARBONE (*Biochem. Zeitsch.*, 1913, **49**, 293—316).—According to the theory of M. Fischer, œdema is due essentially to imbibition of water, which, in the case of proteins, takes place more readily in the presence of alkalis and bases, and is inhibited by salts. The authors discuss the subject of brain swelling from the clinical and pathological point of view, and suggest as a possible cause for the imbibition of water by the brain an increase of acid in the circulation. They have, however, failed to substantiate the hypothesis, as the injection of acids under varying conditions into animals (rabbits) did not produce œdema. S. B. S.

The Fatty Acids of the Human Brain. EGERTON CHARLES GREY (*Biochem. J.*, 1913, **7**, 148—156).—At least 25% of the solid fatty acids of the brain are hydroxy-acids; of these, three have been isolated: $C_{17}H_{34}O_3$ or $C_{22}H_{44}O_4$, m. p. 100—101°; $C_{25}H_{50}O_3$, m. p. 91·0°; and $C_{20}H_4O_3$, m. p. 73·5°, and two at least are mono-hydroxy-acids, and therefore are not produced artificially by oxidation of unsaturated fatty acids. The unsaturated acids include oleic, linoleic, and linolenic acids; also an acid still more unsaturated, to which the name *clupanodenic acid* is given; it combines with 12 atoms of bromine. Another is a solid, $C_{18}H_{34}O_2$ or $C_{18}H_{36}O_2$, m. p. 42°; this is probably an isomeride of oleic acid. The saturated acids are stearic, palmitic, myristic, and Thudichum's neurostearic acid, m. p. 51—52°. The resemblance between the hydroxy-acids of the brain and those of lanoline is additional evidence of the relationship of nervous tissues to other tissues of epiblastic origin.

W. D. H.

Action of Various Influences on the Mammalian Heart V. H. K. MOORHOUSE (*Amer. J. Physiol.*, 1913, **31**, 421—438).— Isolated strips of the cat's auricle beat spontaneously in a bath of oxygenated Ringer's solution; the rhythm and effect of temperature are approximately equal in coronary, nodal, and septal strips. Drugs which act on the vagus are more effective on strips which do not contain nodal muscle. Drugs which act on sympathetic nerve-endings produce an equal effect on all these kinds of strip, but the acceleration lasts longest in septal strips. The sino-auricular node does not exhibit any specially reactive properties to various influences affecting rhythm.

W. D. H.

The Action of Oxalic Acid on the Frog's Heart. OSKAR GROS (*Arch. expt. Path. Pharm.*, 1913, **71**, 395—406).—A solution of sodium oxalate added to Ringer's solution soon stops the heart of the frog in diastole. Its activity is restored by washing out with a calcium-free solution. Sodium citrate acts more powerfully in the same way, although its power to precipitate calcium is less. It is held that the removal of the calcium is not the cause of the action, but that oxalates and citrates have a specific harmful effect on cardiac tissue.

W. D. H.

Diastases. II. Sugar Formation in the Frog's Liver. I. IVAR BANG (*Biochem. Zeitsch.*, 1913, **49**, 40—86).—The experiments were carried out with both *Rana esculenta* and *R. fusca*. Sugar was estimated in separate lobes of the liver. As a rule, one lobe was separated from the others, and the sugar was estimated immediately, whilst the other lobes were allowed to remain in Ringer's fluid and the sugar was estimated after several hours. The amounts of sugar free and existing in the separate lobes from the same animal were also ascertained, and the limits of variation determined. From the alterations in weight after keeping in Ringer's solution, which were found to be small, the conclusion was drawn that the liver still survives even after prolonged keeping in the Ringer

fluid, it being assumed that the organ is not killed, whilst its osmotic properties remain intact. Other reasons are also given for assuming that the organ survives after prolonged immersion in Ringer's solution. After keeping in this liquid, the livers show an increase of reducing sugar (found both in the organ itself and in the fluid in which it is immersed), the amount of which is larger than the variations in the lobes from the same animal. The conclusion was therefore drawn that the surviving liver is capable of producing sugars. The mechanism of this sugar production was studied. It is not due to the diastase of the blood, as there is no appreciable difference between the amounts produced in a liver containing blood and one that has been perfused (from the portal vein). There is, however, a considerable difference between the sugar production by the crushed liver paste and by the intact cells, according to whether the organs have been perfused or not. If they have not been perfused, the paste produces much more sugar, owing to the fact that the diastase of the blood can then act; where they have been perfused, the difference between the sugar production by the paste and intact cells is very much diminished. This is additional evidence of the fact that the sugar production by the surviving liver is not due essentially to the diastase of the blood. The facts indicate that it is due to a liver enzyme. In the case of *Rana esculenta*, the treatment of the liver with alcohol reduces the sugar-producing power of the liver, which can, however, be restored by addition of sodium chloride; in fact, when the liver has been treated in this way, the sugar-producing power is increased beyond that of the original intact liver. This fact is explained by the hypothesis that the alcohol removes some lipoid-like substance which exerts an inhibitory action on the sugar-producing power. As the addition of the alcoholic extract does not inhibit this power exerted by the extracted liver and salt, it is assumed that the inhibitory substances only exert their action when in some form of combination, which is broken up on treatment with alcohol, but not restored on the addition of the alcoholic extract. The same phenomena were not observed in the livers of *R. fusca*, which, unlike those of *R. esculenta*, do not appear to contain a large store of enzyme or pro-enzyme, which can be activated by the addition of salt.   S. B. S.

Diastases. III. Sugar Formation in the Frog's Liver. II. IVAR BANG (*Biochem. Zeitsch.*, 1913, **49**, 81—119).—Adrenaline increases the sugar-producing power of the liver, in quantities which are insufficient to kill the organ. Details are given of Overton's experiments on the irritability of muscles after treatment with adrenaline which justify the conclusion as to the relative non-toxicity of the adrenaline solutions employed. A detailed account is given of the action of adrenaline on the sugar production of the liver under varied conditions. In the case of *R. fusca*, the increased production appears to be due to the reduction of the acidity of the medium, and the effect can be imitated by the use of neutral phosphate solutions. Furthermore, the accelerating effect of the adrena-

line in these cases can be antagonised by the presence of minute amounts of free hydrochloric acid. In the case of *R. esculenta*, the action of adrenaline appears to be exerted on the intracellular lipoids, which in combination inhibit the diastatic action of the organ (compare preceding abstract). The adrenaline action in this case can be imitated by treating the liver with narcotics (for example, alcohol), which can also break down the lipoid complex. There is no evidence that adrenaline causes new production of enzyme; it appears only to activate the pre-existing ferment.

S. B. S.

The Formation of Glycogen from Glyceraldehyde in the Liver. JAKOB PARNAS (*Zentr. Physiol.*, 1912, 26, 671—672).— Perfusion of the tortoise's liver with glyceraldehyde in Ringer's solution leads to the deposition of glycogen therein, at the rate of about 50 mg. reckoned as dextrose per hour per 10 grams of liver. Whether this is due to condensation, or oxidation through the stages of glyceric acid, glycolaldehydecarboxylic acid, and glycol-aldehyde is uncertain; the view that dextrose is katabolised into glyceraldehyde in the body is also unsettled.   W. D. H.

The Importance of Cholesterol in the Organism. LEON-HARD WACKER and WEBNER HUECK (*Arch. expt. Path. Pharm.*, 1913, 71, 373—394).—The methods of estimation of cholesterol are dis-cussed, but the microscopic examination of the adrenal cortex gives a good indication of the amount present. In this situation free cholesterol is an integral and stable cell constituent, but the chole-sterol in the condition of ester is variable and labile. It is here that the polarising microscope is especially useful. In arterial sclerosis, chronic kidney disease, diabetes, and during pregnancy the amount of cholesterol esters increases, but in long-continued infectious disease, septic processes, chronic ulcer, cancer, and tubercle it falls. In the acute stages of infectious diseases, it increases. The amount in the blood varies directly as that in the suprarenal; this is regarded as important, for cholesterol plays a rôle in the natural protective processes of the body.   W. D. H.

The Iodine-containing Complex of Thyreo-globulin. FRED C. KOCH (*J. Biol. Chem.*, 1913, 14, 101—116).—The full activity of thyroid tissue (measured by Hunt's method) is contained in the thyreo-globulin fraction. The full activity per iodine unit is still present in the metaprotein fraction from this globulin, although the iodine in this fraction is increased three-fold. Other products of hydrolysis (proteoses and iodothyrin) show a decrease in activity per unit of iodine. The amino-acid fractions contain very little iodine, and are either inactive or nearly so. Tetra-iodohistidine anhydride and iodotryptophan have no activity.   W. D. H.

Some Phosphatides of Human Placenta. I. and II. C. SAKAKI (*Biochem. Zeitsch.*, 1913, 49, 317—325, 326—332).—The placenta was extracted with alcohol at 60°. A white substance

only sparingly soluble in cold alcohol was isolated, which was very similar in properties to the diaminophosphatide isolated by Thierfelder and Stern from egg-yolk. Its composition was intermediate between that of *apo*myelin and sphingomyelin, as isolated by Thudichum. A preliminary account of other products is given. No evidence as to the existence of jecorin was obtained.

In the second paper, a preliminary account is given of various fractions, none of which can be claimed to be a pure product.

<div align="right">S. B. S.</div>

Muscular Contraction ; Influence of Non - electrolytes, Electrolytes, and Osmotic Pressure. GEORGES KLEEFELD (*Bull. Acad. roy. Belg.*, 1913, 91—180).—The principal views of J. Loeb on the antagonism between calcium ions and those of potassium and sodium, as well as on the toxicity of sodium ions, are confirmed; perfusion with calcium chloride extinguishes muscular excitability; sodium nitrate has the same effect, and potassium is sometimes indifferent; at other times it abolishes excitability. Certain non-electrolytes (sucrose, dextrose) are capable of determining rhythmic contractions. Calcium is sometimes an excitant of contractility, and is able to render contractile muscles treated with sodium citrate. Calcium can exist in the perfusion fluids far above the normal amount without suppressing excitability. By the method of Lapicque-Weiss it can be shown, however, that electrical irritability can diminish, even although the muscle executes normal contractions. Contractility and irritability cannot be regarded as identical.

<div align="right">W. D. H.</div>

Amount of Creatine in Muscles of Various Animals and in Different Types of Muscles. MARIO CABELLA (*Zeitsch. physiol. Chem.*, 1913, 84, 29—38).—Creatine is always present in the muscle tissue of vertebrates. The amount varies with the nature of the muscle; it is most in striped voluntary muscle, less in heart muscle, and least in unstriped muscle. In birds (hens, ducks) the amount of creatine in the breast muscles is considerably larger than that in the limb muscles.

Similar differences in the amount of creatine are found in the individual muscles of any one animal. These differences persist whether referred to the weight of fresh muscle or dried muscle, or expressed as creatine nitrogen in terms of the total nitrogen. This nitrogen factor lies between 3 and 4 for the voluntary muscles of mammals, birds, fishes, and the heart muscle of the ox. It is from 4 to 5 for the breast muscle of birds, and about 1 for the heart muscle of the hen and the smooth muscle of the ox.

Creatine could not be obtained from the muscular tissue of the mantle or the arms of the octopus.

<div align="right">E. F. A.</div>

Muscle-Creatine. Dialysis of Creatine from Dog's Muscle H. T. LEO and PAUL E. HOWE (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xliii ; *J. Biol. Chem.*, 14).—Creatine dialyses out from muscle into water, Ringer's solution, and various strengths of sodium chloride

solution. Hydrochloric acid delayed the diffusion, alcohol increased
it. The experiments offer no definite evidence as to the way in
which creatine is held in the muscle.   W. D. H.

The Action of Potassium Chloride on Frog's Muscle.
RICHARD SIEBECK (*Pflüger's Archiv*, 1913, **150**, 316—324).—Neutral
isotonic solutions of potassium chloride render muscles rapidly inex-
citable; the muscles increase in weight. Even after some hours,
when there is a 20% increase in weight, the action is completely
reversible. Organs the structure of which is destroyed by freezing
and thawing, do not swell in solutions of potassium chloride, but
swell in alkaline solutions. An acid reaction causes in muscle either
in Ringer's or a potassium chloride solution no marked reversible
effect; but the swelling is increased by faradic stimulation, an
alkaline reaction, or by narcosis.   W. D. H.

Connective Tissues of Limulus. HAROLD C. BRADLEY (*Proc.
Amer. Soc. Biol. Chem.*, 1912–13, xl—xli; *J. Biol. Chem.*, 14).—The
cartilage-like tissue yields a sclero-protein which is insoluble in
water and the ordinary solvents. It is insoluble in pepsin hydro-
chloric acid, but digests readily in a tryptic mixture. It gives the
usual protein reactions, but no gelatin was obtained. The white,
fibrous tissue within the carapace is also composed of a non-
collagenous sclero-protein. It digests readily in a peptic, but very
slowly in a tryptic, mixture.   W. D. H.

The Secretion of Pigments by Annelids. K. KSCHISCHKOWSKI
(*Chem. Zentr.*, 1913, i, 40; from *Zentr. Physiol.*, 1912, **26**, 528—532).
—Under certain conditions, *Lumbriconereis impatiens* secretes a
lilac-red pigment, which gives an orange solution in ether and a
pink in chloroform. The secretion is provoked in a specific way by
solutions of potassium salts which are isotonic with a 3·5% solution
of sodium chloride. If the organisms are narcotised or kept in
isotonic solutions free from potassium salts for some time, the
pigment reaction does not occur for several days.   J. C. W.

The Rôle of Glycogen, Lecithides, and Fats in the Repro-
ductive Organs of Echinoderms. BENJAMIN MOORE, EDWARD
WHITLEY, and ALFRED ADAMS (*Biochem. J.*, 1913, 7, 127—141).—The
male and female reproductive glands in echinoderms contain large
amounts of reserve metabolic products, such as glycogen, fat, and
lecithides. These reserves are only slowly used up, if at all, when
the animal is deprived of food. In such glands no sugar forma-
tion occurs in a period of two days after death. The fatty sub-
stances are highly unsaturated, thus resembling liver oils.

W. D. H.

The Basic and Acidic Proteins of the Sperm of Echinus
esculentus. Direct Measurements of the Osmotic Pressure
of a Protamine or Histone. BENJAMIN MOORE, EDWARD WHITLEY,
and ARTHUR WEBSTER (*Biochem. J.*, 1913, 7, 142—147).—A substance

was separated from the ripe male gonads of *Echinus esculentus*, which had properties intermediate between those of a histamine and a histone. Its molecular weight calculated from its osmotic pressure is 8780. Its action on ova and cell division was tested, but the results were negative. W. D. H.

Anoxybiose and Chemical Polarity. (Mme.) ANNA DRZEWINA and GEORGES BOHN (*Compt. rend.*, 1913, 156, 810—812).—*Prostheceraeus* and *Convoluta* when placed in tubes deprived of oxygen for six hours and then returned to aerated water, in all cases exhibit the phenomenon that the anterior extremity has possessed a greater resistance to the privation of oxygen than the posterior extremity, the latter becoming disintegrated when returned to water, whilst the heads live and can be seen swimming about. This differentiation the authors compare with chemical polarity. W. G.

The Composition of Human Bile. ERNST VON CZYHLARZ, ADOLF FUCHS, and OTTO VON FÜRTH (*Biochem. Zeitsch.*, 1913, 49, 120—129).—Details are given for the estimation of the following constituents of the bile: Total solids, pigment (colorimetric method), cholesterol (colorimetric method with chloroform and acetic anhydride), higher fatty acids, mucin, bile acids (as cholic acid). Typical analyses are given of bile obtained from the bladder and from fistulæ. Administration of cholesterol *per os* appeared to increase, not the amount of cholesterol, but that of the bile acids in the bile obtained from a fistula. S. B. S.

Secretin and Vaso-dilatin. L. LAUNOY and KARL OECHSLIN (*Compt. rend.*, 1913, 156, 962—965).—By repeated precipitation by absolute alcohol from aqueous solution the authors have obtained the secretin of Bayliss and Starling (A., 1902, ii, 275, 613; 1903, ii, 316) in a solid state as a non-hygroscopic, white powder, very soluble in water, having an alkaline reaction and a very marked exciting influence on the secretion of pancreatic juice, but no depressing effect. Further, on concentrating the alcohol used for the above precipitation, they obtained a yellow, hygroscopic powder, soluble in water, and having a strongly alkaline reaction. Its aqueous solution only produces feeble secretion excitation, but is strongly depressant. It corresponds with the "depressor substance" mentioned by Bayliss and Starling (*loc. cit.*). This shows that Popielski's vaso-dilatin (compare A., 1912, ii, 593) is distinct from the above secretin. W. G.

An Attempt to Estimate the Vitamine-fraction in Milk. CASIMIR FUNK (*Biochem. J.*, 1913, 7, 211—213) —In milk freed from protein the vitamine fraction is precipitable by phosphotungstic acid; the amount of vitamine ($C_{17}H_{20}O_7N_2$) is about 1 to 2·5 mg. per litre. The filtrate still contains nitrogen, which probably represents allantoin. If milk is freed from fat by the centrifuge, about half the vitamine and allantoin is lost. Both allantoin and vitamine are destroyed by boiling. W. D. H.

The Secretion of the Two Kidneys. RAPHAEL LÉPINE and
RAYMOND BOULUD (*Compt. rend*, 1913, **156**, 754—756). — An
examination of the amount of urine flowing from each of the
kidneys of a healthy dog and a determination of the urea, sugar,
and chlorides present in each case. In every case there was a
greater flow from the right side, and the urine from·this side was
richer in chlorides and sugar. The nitrogen-urea coefficient was
the same for both sides. These differences are stated to be due
partly to a difference in the secretion activity, but principally to
differences in resorption of the urinary constituents by the two
kidneys.   W. G.

The Extremes of Variation of the Concentration of
Hydrogen Ions in Human Urine. LAWRENCE J. HENDERSON and
WALTER W. PALMER (*J. Biol. Chem.*, 1913, **14**, 81—85).—After a
dose of 10 grams of monosodium phosphate there is a slight increase
of hydrogen ion concentration in the urine. Larger quantities of
acid phosphate or of hydrochloric acid produce a similar effect, but
the acidity is never as great as in many pathological conditions. A
more alkaline urine is produced by sodium hydrogen carbonate, but
beyond a certain point even after large doses of alkali the reaction
of the urine does not change. In a large number of observations
the highest acidity exceeded 4·70; the highest alkalinity 8·70. This
corresponds with a range of 1:10,000 in the concentration of
hydrogen and hydroxyl ions. The actual variation in normal people
is at least 0 5 gram-molecule. In pathological states the variation
is greater. In most acid urines, the urinary acids are in large
measure free; in most alkaline urines they are almost completely
combined with bases.   W. D. H.

Diastase in the Urine of Infants. ERNST MAYER (*Biochem.
Zeitsch.*, 1913, **49**, 165—167).—Diastase is seldom completely absent
from the urine of breast-fed children. In the first three months,
however, it does not exceed 5 units (in Wohlgemuth's system).
There is no appreciable increase in the next three months. Between
the sixth and ninth month the values vary between 2·5 and more
than 20 units, after which period higher values are obtained. The
amount is, however, affected by pathological complications.
                                                           S. B. S.

Excretion of Purine Katabolites in Sundry Types of Mam-
malia. MAURICE H. GIVENS and ANDREW HUNTER (*Proc. Amer. Soc.
Biol. Chem.*, 1912—13, xxiv—xxv; *J. Biol. Chem.*, **14**).—Allantoin
is a regular constituent of the urine of rabbit, horse, pig, cow, cat,
dog, coyote, monkey, and man. To this list may be added the
opossum, guinea-pig, porcupine, sheep, and racoon. In man the
figure is smallest. Uricolytic power is greatest in carnivora; then
follow rodents, ungulates, and marsupials in the order named. It
is practically absent in man.   W. D. H.

Estimation of Amylolytic Ferments in the Urine as a
Measure of Certain Pathological Conditions. DUDLEY CORBETT
(*Quart. J. Med.*, 1913, **6**, 351—383).—The amount of ferment passed

by a given individual in twenty-four hours' urine is fairly constant, varying between 6·6 and 33 Wohlgemuth units, the average being 10—20°. It is also present in blood serum, the average amount being 10 units. The quantity in the urine is unaffected by the diet, the reaction of the urine, the presence of bacteria, and other abnormal constituents, with the exception of blood. The amount in the urine does not appreciably diminish if the urine is kept in the presence of toluene. The amount in the urine of an infant fed on milk is very small, but rises on the administration of starchy food. When the amount of ferment in the serum exceeds that of the urine, there is a renal deficiency, as the ferment is readily excreted by normal kidneys. High readings were never obtained in pure cases of renal disease. High readings (up to 100 or even more) were found in certain acute infective conditions, in pancreatic disease, in certain forms of eclampsia, and in one case of " acidosis " in a child. All cases of undoubted pancreatic disease, whether due to malignant or inflammatory processes, gave high readings, and the test may therefore be of value for diagnosis of such conditions. In diabetics on strict diet, the readings were generally subnormal. In severe cases the readings were lower than in the milder forms, but in these conditions the excessive amount of urine excreted must be taken into account. S. B. S.

Sarcolactic Acid and the Theory of Diabetes. R. T· WOODYATT (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxxviii ; *J. Biol· Chem.*, 14).—A theory is proposed that the internal secretion of the pancreas dissociates dextrose and perhaps other hexoses, and that the presence of lactic acid is evidence of such dissociation. In pancreatic diabetes there is lessened dissociation and less lactic acid in the tissues. W. D. H.

The Behaviour of Blood Sugar in Normal and Pathological Cases. VII. The Blood Sugar in Diabetes Mellitus. FR. ROLLY and FR. OPPERMANN (*Biochem. Zeitsch.*, 1913, 49, 278—292. Compare this vol., i, 425).—No direct relationship was found between the amount of blood-sugar and glycosuria in diabetes. It was found that only in the case of severe diabetes did ingestion of proteins cause a rise both of blood-sugar and glycosuria. The blood sugar content did not increase either in the case of carnivora (dogs) or herbivora after administration of proteins. The administration of meat and carbohydrate foods caused a greater amount of glycosuria in diabetics than a similar diet in which the meat was replaced by vegetable proteins. S. B. S.

Sulphur Metabolism. I. The Urinary Sulphur Partition in Various Diseases. N. STADTMULLER, MAX KAHN, and JACOB ROSENBLOOM (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xliv; *J. Biol. Chem.*, 14).—High proportions of neutral sulphur were passed in nearly all cases of diabetes, in all cases of cancer, in one case of nephritis (out of two), and in the one case examined of hypopituitarism. W. D. H.

The Intestinal Flora. The Possible Production of Ptomaines in Acid Medium. ALBERT BERTHELOT and D. M. BERTRAND (*Compt. rend.*, 1913, **156**, 1027—1030. Compare A., 1912, ii, 668).—*Bacillus aminophilus intestinalis*, sown on media containing histidine and peptone, to which were added, instead of dextrose, amounts of lactic acid varying from 0·5 to 5 per 1000, shows marked culture and formation of 4-β-aminoethylglyoxaline, even with 3 per 1000 of acid present. Thus, in the intestinal flora of persons exhibiting, at the same time, symptoms of enteritis and colitis, their fæces being acid, the *B. aminophilus* may be found capable of attacking histidine even in a slightly acid medium. This bacterium is capable of acting in the intestine as a simple lactic ferment without forming any toxic base, but it can, in certain cases, produce aminoethylglyoxaline equally well in neutral or alkaline medium, or in the presence of acids elaborated by other microbes, and its attack is not limited solely to histidine.   W. G.

The Action of Aloin on Metabolism. The Physiology of Artificially Produced Gout and Fever. M. BERRÁR (*Biochem. Zeitsch.*, 1913, **49**, 426—446).—It has already been shown by Kossá, that administration of aloin to birds produces increased output of uric acid, which, in cases where the action of the kidneys is inefficient, leads to the production of an artificial gout. The researches on aloin have now been extended to mammals. Quantities of 0·1 to 0·2 gram per kilo. of body weight, administered to dogs, produces an increase of temperature and increased metabolism, which at the height of action can be double the normal. Both the gaseous metabolism and the output of various products in the urine and fæces were investigated. The substances forming the source of the increased energy production were those most readily at the disposition of the organism at the time of the administration of the drug. In the starving animal, the fat and proteins served chiefly for this purpose, whereas in the case of an animal which had received a diet rich in carbohydrates, these substances were mostly drawn upon, their metabolism increasing from 150 to 500%, the normal value. No distinct relationship was ascertained between the amounts of different products employed to meet the increased energy needs.   S. B. S.

Use of the Oxydase Reaction in the Differentiation of Acute Leucæmias. JOHN SHAW DUNN (*Quart. J. Med.*, 1913, **6**, 293—308).—The occurrence of a positive indophenol-oxydase reaction in large, non-granular cells in acute leucæmia is a certain proof of their myeloid nature, and enables a diagnosis of acute myeloid leucæmia to be readily made from a blood examination. The reaction is negative in the more embryonic forms of marrow-cells, and in small myoblasts, and is probably always negative in the most typical stage of large myoblasts with uniformly dense basophil reticular protoplasm. When the reaction is positive in these large, non-granular cells, it is associated with alterations in the protoplasm, which are recognisable by ordinary staining

methods, and indicate stages of ripening towards the granular myelocytes. Cases of acute myeloid leucæmia may occur in which the type of blood-formation is so embryonic that the oxydase reaction is valueless for differential diagrams; but even in such cases the histological characters of the large leucocytes may render a diagnosis possible. S. B. S.

Narcosis. BRUNO KISCH (*Zeitsch. Biol.*, 1913, **60**, 399—456).— The action of photodynamic materials (eosin, methylene-blue) is increased in *Colpidia* by the addition of alcohol, ether, or chloroform. Dilute alcohol, however, acting for short periods, sometimes has the opposite effect so far as eosin is concerned. Narcosis in these animals is markedly affected by light. In *Spirostomum* the action of increased oxygen tension is increased by light, and there is a rise in the oxygen consumed in *Oʃalɪno*. The effect of light and oxygen on *Spirostomum* is inhibited by narcotics, but this is not seen in *Opalina*. The movements of these animals are paralysed by narcotics, but not in a reversible way. W. D. H.

Gastric Juice in Malignant and Non-malignant Diseases of the Stomach and Duodenum. SAMUEL B. SCHRYVER and CHARLES SINGER (*Quart. J. Med.*, 1912, **6**, 71—81; 1913, **6**, 309—350).— Hans Fischer and Neuberg have suggested that the capacity of gastric juice to hydrolyse glycyl-tryptophan is diagnostic of cancer. The authors have investigated the action of gastric juices on Witte's peptone, and have shown, by the use of Sörensen's formaldehyde titration method, that in certain cases the gastric juice contains a peptolytic ferment. This was found in about $6\frac{1}{2}\%$ of the cases examined, all of which were taken from patients suffering from grave gastric disorder. It is only found when free hydrochloric acid is absent, and where the peptic powder is low, or even absent. It is not diagnostic of malignancy, as in the majority of cases of undoubted cancer the ferment was absent. It is most commonly associated with gastric dilatation and atrophy of the walls of the stomach, and is probably of intracellular origin.

Investigations were also carried out with the object of interpreting the analyses of gastric juice as regards the titration numbers obtained when methyl-orange and phenolphthalein are used as indicators. If B denotes the number of c.c. of $N/10$-sodium hydroxide necessary to neutralise 10 c.c. of gastric juice to phenolphthalein, and C the number of c.c. of alkali required to neutralise the same amount to methyl-orange, and A the number of c.c. of $N/10$-ammonia produced when 10 c.c. of the juice are incinerated by Kjeldahl's method with sulphuric acid, then $(C-B)/A$ was found to be a constant for any given amino-acid or mixtures of amino-acids or digestion products. $(C-B)/A \times 10$ has been designated the "nitrogen factor," and this is approximately a constant, and equal to about 2·4 for all cases of normal gastric juice. It is higher than that of gluten which has been digested for about one hour with pepsin in $N/20$-hydrochloric acid and pepsin of the same strength as that normally found in gastric juice, but is about equal to that

of a digest of an Ewald test-meal produced under similar conditions. The results indicate that the hydrochloric acid is not excreted in the form of an organic precursor. In cases of pyloric obstruction the "nitrogen factor" rises to 2·8 and more, and these high numbers are practically diagnostic for this condition. In cases of carcinoma of the body of the stomach, free mineral acid is absent, and pepsin is almost always absent, the analyses indicating almost complete achylia. In ulcers of the body of the stomach, the analyses vary, but complete achylia, such as is found in cases of carcinoma, is infrequent. Sometimes the analyses in this condition are not far removed from normal. In cancer of the pylorus, as opposed to cancer of the body of the stomach, the analyses are generally nearly normal; it is only when this condition is accompanied by distension and obstruction that the analytical numbers are sub-normal. The composition of the juice appears therefore to be affected rather by the site than the character of the lesion. Analytical numbers higher than normal are characteristic of pyloric and duodenal ulcers. Attention is called to the value of pepsin estimations, and to certain low values of the pepsin, when the hydrochloric acid secreted is normal or even high. For the purpose of pepsin estimation, the Fuld-Levison edestin method was employed.   S. B. S.

The Entrance of Iodine into Diseased Tissues. H. GIDEON WELLS and O. F. HEDENBURG (*Proc. Amer. Soc Biol. Chem.*, 1912–13, xxxvi—xxxvii; *J. Biol. Chem.*, **14**).—Necrotic tissues, whether caused by tuberculosis or not, are more permeable to iodine, and therefore contain more than healthy tissues when iodine is given. W. D. H.

Pharmacological Investigations of Ammonium Chloride. RODOLFO MENEGUZZI (*Chem Zentr.*, 1913, i, 1046; from *Arch. Farmacol. sperim.*, 1912, **14**, 411—420).—The injection of ammonium chloride into the veins of a rabbit caused a retardation in the pulse-beats and an increase in the blood pressure, whilst the breathing was quickened at first, but suddenly ceased. A 1/40N-solution had a toxic action on the fresh gastrocnemius of a frog, but weaker solutions were without effect.   J. C. W.

Behaviour of Mercury [in the Organism]. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **84**, 67—68).—Polemical. Compare Buchtala (this vol., i, 318).   E. F. A.

The Injection of Salts of Radium. HENRI DOMINICI, (Mme.) SIMONE LABORDE, and ALBERT LABORDE (*Compt. rend.*, 1913, **156**, 1107—1109).—A study of the intravenous and intramuscular injection of soluble and insoluble salts of radium, which shows that they persist for a long time in the organism. In the case of the insoluble salts injected into the muscles the greater portion of the radium remains at the point of injection, whereas with the soluble salts it is diffused throughout the organism. The bony tissue retains an appreciable quantity of the radium injected as radium bromide, thus bringing radium into line with calcium and strontium in this respect.   W. G.

Thorium-X in Biology and Pathology.   J. PLESCH, LÁSZLÓ KAROZAG, and BRUNO KEETMAN (*Chem. Zentr.*, 1913, i, 318, from *Zeitsch. exper. Path. Ther.*, 1912, **12**, 1—84).—The behaviour and distribution of thorium-X in the animal organism are described. The measurements were made by estimating the α- or γ-radiation. About 80% is retained in the body, roughly two-thirds being stored in the bones, and most of the remainder in the liver.   The toxicity varies considerably for different animals, and a lethal dose for a man is calculated at 10,000 electrostatic units, whilst a therapeutic dose should not exceed 1000 units.   The symptoms accompanying the administration of thorium-X vary.   The respiration of healthy subjects is not affected, but in cases of cardiac weakness or pneumonia the blood pressure is reduced.   The preparation has a clinical application in metabolism, circulation and blood troubles, and in infectious diseases.   J. C. W.

Action of Thorium-X on the Circulation.   THEODOR A. MAASS and J. PLESCH (*Chem. Zentr.*, 1913, i, 318; from *Zeitsch. exper. Path. Ther.*, 1912, **12**, 85—94).—Experiments on the isolated heart of a frog show that, like radium emanation, thorium-X increases the diastolic relaxation of the heart.   J. C. W.

Experimental and Histological Investigation of the Action of Thorium-X on the Animal Organism.   A. PAPPENHEIM and J. PLESCH (*Chem. Zentr.*, 1913, i, 318; from *Zeitsch. exper. Path. Ther.*, 1912, **12**, 95—107).—The results of the action of thorium-X on the animal organism are to be referred to dilation of the blood vessels accompanied by bleeding and poisoning of the cells.   Thorium-X is also a poison to the leucocytes of the marrow of the bones and to the kidney and liver epithelia.   J. C. W.

Pharmacological Differences between *cis*- and *trans*-Isomerides.   HEINRICH DRESER (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913, 122—123).—The following figures give before the / the lethal dose, and after the / the dose which is no longer lethal, in the case of frogs (F) and white mice (M).   The doses were injected under the skin, and are given in percentage-weights of the animal used.   Atropic acid, F, 0·45/0·40; M, 0·0054/0·0022.   Ordinary cinnamic acid, F, 0·30/0·25; M, 0·19/0·166.   *allo*Cinnamic acid, F, 0·46/0·42; M, 0·2/0·175.   *trans-o*-Coumaric acid, F, 0·45/0·40; M, 0·30/0·278.   *cis*Coumarinic acid, F, 0·084/0·0745; M, 0·01/0·0051.   *trans-o*-Methoxycinnamic acid, F, 0·20/0·15; M, 0·07/0·04.   *cis-o*-Methoxycinnamic acid, F, 0·7/0·5; M, 0·15/0·111.

The lethal doses are smaller for warm-blooded than for cold-blooded animals (compare atropic acid).   The *cis*-isomeride is less poisonous than the *trans*-isomeride; the exception shown by coumaric and coumarinic acids is due to the fact that the latter gives the very poisonous coumarin in the organism.   The introduction of phenolic hydroxyl into the ortho-position in *trans*-cinnamic acid decreases, whereas the methoxy-group increases, the toxicity.

The results show that no assumptions as to the pharmacological action of a substance can be based on chemical isomerism.

                                                                    T. S. P.

Pyruvic Acid Glycosuria. II. The Question of Sugar Formation from Pyruvic Acid. PAUL MAYER (*Biochem. Zeitsch.*, 1913, **49**, 486—501).—If pyruvic acid in suitable doses is administered to rabbits and dogs with total phloridzin diabetes, it causes an injury to the kidneys, which are rendered less permeable to nitrogenous substances and sugar. The administration in these cases results therefore in a diminution of both sugar and nitrogen in the urine. Even in cases where no injury to the kidneys could be ascertained, the administration of pyruvic acid led to no extra output of sugar. The experiments with animals with phloridzin diabetes offer, therefore, no solution of the problem as to whether pyruvic acid can be regarded as a sugar former in the body.

                                                                    S. B. S.

The Action of Methyl Alcohol on the Circulating Blood. SOICHIRO MIURA (*Biochem. Zeitsch.*, 1913, **49**, 144—151).—In two only out of five experiments (on four rabbits and one dog) did injection of methyl alcohol produce anæmia. There was observed a diminution of lymphocytes and an increase in the number of pseudo-eosinophile or neutrophile corpuscles and also hæmoglobinuria. The methyl alcohol appears to act toxically on the blood-forming apparatus.   S. B. S.

Caffeine Hyperglycæmia. THOR STENSTROM (*Biochem. Zeitsch.*, 1913, **49**, 225—231).—It has been assumed that caffeine preparations produce glycosuria by acting on the kidneys. If this is the case, then no hyperglycæmia should result. The author now shows, by experiments on rabbits, employing Bang's microchemical method of sugar estimation, that administration of caffeine derivatives leads to increase of sugar in the blood, which commences about an hour after administration, rises to a maximum and then falls. In two cases, after the maximum period there was a second very rapid rise and fall, which was accompanied by convulsions in the animals, which subsequently died. The conclusion is drawn that the glycosuria produced by caffeine preparations is not due to the action on the kidneys.   S. B. S.

The Behaviour of Dextrose-Resorcinol in the Animal Organism. LUCIANO PIGORINI (*Chem. Zentr.*, 1913, i, 319; from *Arch. Farmacol. sperim.*, 1912, **14**, 353—358).—The additive compound of dextrose and resorcinol (Fischer and Jennings, A., 1894, i, 397) is without harm to the frog or the guinea-pig, and is excreted unchanged, whereas resorcinol or mixtures of resorcinol and dextrose have a toxic action.   J. C. W.

The Destruction of α-Hydroxypropaldehyde and Methyl-glyoxal by Animal Organs. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **49**, 502—506).—It has been suggested that pyruvic

acid, as an intermediary product of sugar fermentation, can be formed by the Cannizzaro reaction from methylglyoxal. Equations are given showing that this substance can yield on hydrolysis (1) pyruvic acid and acetol, or (2) pyruvic acid and α-hydroxypropaldehyde, (3) pyruvic acid only. It was therefore of interest to investigate the behaviour of methylglyoxal and α-hydroxypropaldehyde when these substances are treated with various ferments from yeast or animal organs. Experiments show that with liver paste, both substances are destroyed, the former more rapidly than the latter. p-Nitrophenylhydrazine acetate was employed to detect their presence in the mixture, after the proteins had been precipitated by colloidal ferric hydroxide. More lactic acid was found in the incubation mixture than the organs alone would yield. The actual course of the reactions discussed has not, however, been yet entirely elucidated. S. B. S.

The Behaviour of Ferric Iodoparanucleate in the Organism. ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1913, **49**, 152—164).—By the action of iodine on ferric paranucleate (triferrin), a product can be obtained which contains about 8% of organically combined iodine. It causes no toxic symptoms when administered to dogs and rabbits. On administration *per os*, the iodine, even in large doses, is completely absorbed into the system, whereas the iron is only partly absorbed. The iron content of the liver can be increased threefold after administration of iodotriferrin. No organically combined iodine could be detected in the body, after ingestion of the medicament, and the iodine appears to be excreted chiefly as alkali iodide, with a small quantity as an iodo-derivative of an aromatic acid. The iodine excretions last for three days after administration of the drug. S. B. S.

Enzyme Concerned with the Formation of Hydroxy-acids from Ketonic Aldehydes. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, **14**, 155—157).—Phenylglyoxal administered to rabbits in doses of 1—1·5 grams per kilo. leads to the excretion of about half a gram of optically active *l*-mandelic acid and about 0·75 gram of hippuric acid. No phenylglyoxylic acid was detected. Aqueous extracts of various animal tissues contain an enzyme capable of converting phenylglyoxal into mandelic acid, the action of which is readily inhibited by heat.

By analogy, methylglyoxal should be converted into lactic acid, and an enzyme extract prepared from dog's liver is shown to effect this change.

Phenylglyoxal readily combines with histidine, arginine, ornithine, and lysine to give sparingly soluble yellow substances. E. F. A.

The Influence of Phloridzin on Dogs with Eck's Fistula. JOSHUA E SWEET and A. I. RINGER (*J. Biol. Chem.*, 1913, **14**, 135—138). —Phloridzin produces glycosuria in dogs with Eck's fistula exactly as in normal dogs. The power of gluconeogenesis is not lessened. W. D. H.

The Influence of Phloridzin on a Splenectomised Dog. JOSHUA H. AUSTIN and A. I. RINGER (*J. Biol. Chem.*, 1913, **14**, 139—140). —In dogs minus a spleen the effect of phloridzin exactly resembled those produced in normal animals.   W. D. H.

Lead Compounds in the Organism. ANTONIO RIVA (*Chem. Zentr.*, 1913, i, 1047—1048 ; from *Arch. Farmacol. sperim.*, 1912, **14**, 406—410).—The lead-poisoned liver of a dog was extracted by physiological salt solution, and the filtrate, containing the albumins, globulins, and nucleoproteins, was evaporated to dryness. Lead was only found in the globulin, apparently in combination, since it persisted after repeated dialysis. A globulin from horse serum showed a great affinity for lead.   J. C. W.

The Action of Dyes in Conjunction with Poisons and Medicaments. JOSEF SELLEI (*Biochem. Zeitsch.*, 1913, **49**, 466—478). —The mixture of dyes with poisons increases in many cases the toxicity of the latter, even although the dye is by itself practically inert. The dyes chiefly used were vitalneugelb, chrysoidin, methyl-orange, etc., which were combined with, amongst other substances, mercuric chloride, gold chloride, platinum chloride, and other metallic chlorides. Sodium vanadate mixed with a certain quantity of eosin is very toxic, but an increase of eosin in the mixture above a definite limit appears to diminish the toxicity. Other combinations of dyes with metallic poisons are less toxic than the metallic poisons alone. The influence of methylene-blue on the toxicity of copper salts was investigated. The most toxic of these, namely, cupric chloride, loses its toxic power most readily on mixture with the dye, whereas potassium cupric tartrate, which is the least toxic, acts in the presence of methylene-blue most toxically. The mixtures of dyes with the copper salts produce convulsions in the animals (guinea pigs); they also act as strong irritants at the place of injection. The author discusses the theory of the action of dyes.   S. B. S.

Influence of Poisons on the Isolated Heart of the Fish W. I. BERESIN (*Pflüger's Archiv*, 1913, **150**, 549—568).—The heart of the fish (hake) lends itself very well to physiological experimentation. Details are given of the method employed for isolating the heart, and the perfusion apparatus (a modification of Locke's) employed. If poisons are added to the perfusion fluid (Locke's fluid) their effects are readily observable. The poisons used were strophanthine, erythrophlein, caffeine, adrenaline, nicotine, pilocarpine, chloroform, ether, hydrocyanic acid, quinine, and veratrine. The effects are practically identical with those already known from work on the heart of the frog or the mammal; a few differences of detail were noted in one or two instances.   W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Phosphorus Compounds formed by Amylomyces Rouxii. R. GOUPIL (*Compt. rend*, 1913, **156**, 959—962).—*Amylomyces Rouxii* contains combined phosphorus in three states, two organic and one inorganic. The organic compounds are normal constituents of the living tissue, and their formation corresponds with the period of active growth. Of these two compounds one only is soluble in, and extracted by, ether, and is of a lecithin-like nature, whilst the second, which can be extracted by sodium hydroxide and reprecipitation by acids, possesses all the properties of a nucleic acid, and appears to be built up from the lecithin compound. The inorganic phosphates result from the degradation of the organic phosphorus compounds as the plant grows old.   W. G.

The Precipitation of Calcium Carbonate in the Sea by Marine Bacteria. G. HAROLD DREW (*J. Marine Biol. Assoc.*, 1913, **9**, 479—524).—The large, chalky, mud flats forming the Great Bahama Bank, and those near the Florida Keys, are now being precipitated by the action of *B. calcis* on the calcium salts dissolved in sea water. This or similar bacteria may have been an important factor in the formation of various chalk strata and oolitic rocks in addition to the part played by shells of foraminifera, etc. If this is correct, these strata must have been precipitated in shallow seas at tropical temperature. Bacterial denitrification is also far more rapid in tropical than in temperate waters; hence plankton and algæ growth is relatively scarce in the former. More extensive observations on the distribution of bacteria at different places and depths are, however, necessary.   W. D. H.

Alcoholic Fermentation of Lactic Acid. PIERRE MAZÉ (*Compt. rend.*, 1913, **156**, 1101—1104).—A study of the fermentation of lactic acid by a bacillus, capable of fermenting sugars and polyatomic alcohols, and comparable in its physiological properties to the *B. ethacetosuccinicus* of Frankland and Frew (T., 1892, **61**, 254). An examination of the results points to two parallel fermentation processes taking place on the lactic acid:

(1) $C_3H_6O_3 + O = CH_3 \cdot CO_2H + H \cdot CO_2H.$
(2) $C_3H_6O_3 = C_2H_5 \cdot OH + CO_2.$
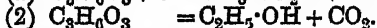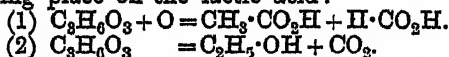
The ratio of acetic acid to formic acid in the product is, however, as 5:1, the alcohol formed in (2) undergoing further oxidation, and this is confirmed by the value of the respiratory quotient. No pyruvic acid could be detected in any of the cultures at any stage.   W. G.

An Acid-producing Enzyme in Bacterium lactis acidi. E. G. HASTINGS and EDWIN B. HART (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xxxviii—xxxix; *J. Biol. Chem.*, **14**).—The enzyme in question acts on lactose, and the acid produced is probably lactic.   W. D. H.

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Employment of Lactic Acid and Lactic Acid Bacteria in the Pickling of Cucumbers. ALEXANDER KOSSOWICZ [with L. VON GRÖLLER] (*Chem. Zentr.*, 1913, i, 640; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, **2**, 78—80).—The presence of small quantities of lactic acid in cucumber sap or asparagine-sugar solutions prevents the development of bacteria of the *Mesentericus* group.   J. C. W.

A New Thermophilic Bacterium. ADOLF AMBROŽ (*Centr. Bakt. Par.*, 1913, ii, **37**, 3—16).—A sporogenous, facultative anaerobic organism, *Denitrobacterium thermophilum*, was obtained from soil and found to have the capacity of growing vigorously at 60—70°, and of decomposing nitrates with the liberation of free nitrogen. Analysis of cultures in nutrient bouillon, containing 0·5% potassium nitrate, showed that about 25% of the total nitrogen was lost during an incubation period of fourteen days at 60—65°. The gases were found to consist of nitrogen and oxides of nitrogen, the former being partly derived from the organic nitrogen compounds in the bouillon.   H. B. H.

The Mechanism of Alcoholic Fermentation. ALEXANDER VON LEBEDEV (*Ber.*, 1913, **46**, 850—851).—Polemical. A reply to Kostytschev (this vol., i, 323), stating that there is nothing essentially new in the latter's views.   D. F. T.

The Rate of Fermentation by Growing Yeast Cells. ARTHUR SLATOR (*Biochem. J.*, 1913, **7**, 197—203).—Various methods for estimating the rate of growth and fermentation are given, some of which are possible when the organism is growing on a solid medium. The rate of growth developing in wort-gelatin follows the logarithmic law.   W. D. H.

Chemical Composition and Formation of Enzymes. VIII. Simultaneous Variation in Amount of Invertase and Fermenting Enzyme in Living Yeast. HANS VON EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1913, **84**, 97—108. Compare A., 1912, ii, 376, 970).—As the result of the previous treatment of the yeast in solutions containing mineral salts and sucrose or invert sugar there is an increase in the inverting power. This change cannot be regarded as an adaptation to environment, since the increase is the same whether the previous treatment is with sucrose or invert sugar. Neither is it due to a general increase in the vital activity of the cell, since the treatment materially lessens the fermentative activity. It is regarded as a special property due to causes as yet unknown.   E. F. A.

The Enzymes of Washed Zymin and Dried Yeast (Lebedev). I. Carboxylase. ARTHUR HARDEN (*Bio.-Chem. J.*, 1913, **7**, 214—217). —If zymin and Lebedev's dried yeast are washed free from co-enzyme they are incapable of fermenting dextrose, but they readily decompose pyruvic acid into carbon dioxide and acetaldehyde, provided that the acidity of the solution is kept low.
        W. D. H.

Action of Free Ammonia on Yeast. Comparison with Other Bases. THOMAS BOKORNY (*Chem. Zentr.*, 1913, i, 641—642; from *Allg. Brauer Hopfen Zeit*, 1912, 52, 2867—2869).—Seeds of cress, barley, wheat, hemp and vetch, and peas and scarlet runners were allowed to germinate in ammonia solutions from 0·1 to 0·01%. Only at the lower dilution did germination proceed, and even then, at a slower rate than in control experiments. Ammonia to the extent of 0·5% in a good culture solution prevented the growth of yeast, whilst potassium hydroxide in the same dilution had no effect. Yeast apparently combines with ammonia, for it was found that 12 grams of yeast with a dry weight of 3·6 grams contained 0·374 gram of the base. Hydroxylamine and phenyl-hydrazine hydrochlorides were poisonous to yeast in 0·1% solutions, whilst hydrazine hydrate in 0·002% and phenylhydrazine in 0·001% solutions entirely prevented any fungoid growth. J. C. W.

Microchemical Detection of Potassium in Yeast and Other Cells. THOMAS BOKORNY (*Chem. Zentr.*, 1913, i, 640—641; from *Allg. Brauer Hopfen Zeit.*, 1913, 52, 113—114).—In order to make the potassium cobaltinitrite precipitate more visible it is blackened by means of ammonium sulphide. It is possible to detect one part of potassium in 5000 at 8° by this method. Potassium could only be found in the cell sap of yeast, but the conclusion is not to be drawn that it is not present in the protoplasm or nucleus in the form of a potassium protein compound. Potassium is necessary for the development of yeast. J. C. W.

Action of Certain Metallic Salts on the Development of Yeast and the Germination of Barley. THOMAS BOKORNY (*Chem. Zentr.*, 1913, i, 641; from *Allg. Brauer Hopfen Zeit.*, 1912, 52, 1905—1906).—The reproduction of yeast was not influenced by the presence of even 4% of potassium dihydrogen phosphate in the culture solution, neither did the ash contain more phosphorus. Cæsium sulphate was found to be harmful to barley seedlings, even in the dilution of 0·05%, but 0·01% of that salt or 0·2% of rubidium sulphate proved to be beneficial, whilst potassium chloride in 0·05% solution did not accelerate germination, and in strong solutions was injurious. J. C. W.

Action of Uranium, Molybdenum, and Vanadium Salts on Yeast and Other Micro-organisms. THOMAS BOKORNY (*Chem. Zentr.*, 1913, i, 641; from *Allg. Brauer Hopfen Zeit.*, 1912, 52, 709—710. Compare A., 1912, ii, 1201).—During fermentations in presence of ammonium molybdate, the liquid acquired a blue colour, due to the action of that salt on hydrolysis products of sucrose, particularly on lævulose. J. C. W.

Influence of Different Substances on the Germination of Vegetable Seeds. I, II, and III. THOMAS BOKORNY (*Biochem. Zeitsch.*, 1913, 50, 1—48, 49—86, 87—118).—Potassium chloride is somewhat injurious to plants in 0·25% solutions, whilst the nitrate

is very injurious in 1% solutions, and may retard growth even in
0·1% solutions. Calcium nitrate (1%) is only slightly injurious, and
sodium nitrate somewhat more so; 0·1% solutions of both salts are
without injurious effects. Even 0·1% solutions of ammonium
nitrate retard germination. Whilst rubidium sulphate is only
slightly injurious in 0·5% solutions, cæsium and lithium sulphates
are injurious in 0·1 and 0·05% solutions respectively.

Germination is quickened by cæsium, lithium, and rubidium
sulphates in 0·01, 0·05, and 0·2% solutions respectively. The
germination of barley was promoted by 0·005% of carbon
disulphide; beans and lentils by 0·01% potassium chromate; cress
by 0·0005% mercuric chloride; barley and cress by 0·0025% and
0·005% copper sulphate respectively; cress by 0·005% of phenyl-
hydrazine; barley and cress by 0·0025% of aniline; barley by 0·01%
of hydroxylamine; and peas, lentils, and barley by 0·001% of
hydrofluoric acid.

It would seem that most poisons stimulate growth when diluted
to certain points. Since a slight increase in concentration causes
injury and a slightly increased dilution renders the substances
inactive, it is doubtful whether this property of poisons can have
any practical importance.   N. H. J. M.

Action of Manganese Dioxide and of Other Metallic Com-
pounds on the Germination of Seeds. UGO VARVARO (*Chem.
Zentr*, 1913, i, 546—547; from *Staz. sperim. agrar. ital.*, 1912, 45,
917—929).—The oxides of manganese, iron, uranium, cerium,
copper, zinc, aluminium, cadmium, and mercury hinder the germina-
tion of beans, and are poisonous, even in small doses, to horse
beans. The oxides of zinc, lead, copper, cadmium, aluminium, and
uranium are stimulants to maize.   J. C. W.

Formation of Pentosans in the Germination of Seeds.
LUIGI BERNARDINI and F. GALLUCCIO (*Chem. Zentr.*, 1913, i, 179; from
Staz. sperim. agrar., ital., 1912, 45, 874—884).—The pentosans
developed by seeds germinating in the dark and in the light have
been estimated by Tollens's and Krüger's phloroglucinol method, and
the cellulose by König's glycerol-sulphuric acid method. The
results show that the production of pentosans is slow in the dark,
but rapid in the light, whilst the cellulose content rises at first in
the dark, only to fall off rapidly as germination proceeds, but
increases steadily in the light.   J. C. W.

Respiration of Plants as Hydrolytic Oxidation. VLADIMIR
I. PALLADIN (*Ber. deut. botan. Ges.*, 1913, 31, 80—82).—Alkaline
solutions of the respiration chromogens absorb atmospheric oxygen
vigorously with production of brownish-red pigments. During
alcoholic fermentation, hence in the first anaerobic stage of respira-
tion, substances are formed which readily give up their hydrogen
to the respiration pigment, by which it is oxidised to water by means
of atmospheric oxygen.

The respiration chromogens, like the leuco-compounds, give up

their hydrogen to the absorbed oxygen, producing a pigment and water. The oxygen absorbed during respiration is employed, therefore, as previously shown, in removing hydrogen from the plants.

The hydrogen liberated after the hydrolytic oxidation of dextrose, which in higher plants is oxidised to water and in yeast is eliminated as ethyl alcohol, is given up by anaerobic bacteria to the surrounding gaseous medium.   N. H. J. M.

Causes of Growth of Plants. G. A. BOROVIKOV (*Biochem. Zeitsch*, 1913, 50, 119—128. Compare this vol , i, 324) —Salts which are readily hydrolysed are favourable to growth owing to the presence of acids, and consequently of hydrogen ions. The weaker the base the more easily is it hydrolysed, and the stronger the action of the salt. In solutions of salts of strong organic bases, growth is not quickened because hydrolysis is less, and because such bases have a greater retarding effect than weak bases, such as caffeine, carbamide, and glycine. The quickening or retarding of growth seems to be due to unequal degrees of hydration of the plasma colloids. The conditions which are favourable to the ionisation of the protein also bring about greater hydration of the plasma colloids. Acids are favourable to plants, whilst metals and bases diminish the protein ionisation by neutralising the protein.   N. H. J. M.

Formaldehyde and Plant Syntheses. HERMANN DECKER (*Annalen*, 1913, 396, 336).—The hypothesis of the action of formaldehyde as a methylating agent in the formation of plant substances, advanced by Decker and Becker (this vol., i, 291), was suggested by Pictet eight years ago.   C. S.

Plants which Require Sodium. WINTHROP J. V. OSTERHOUT (*Bot. Gaz.*, 1912, 54, 532—536).—Sodium was found to be as necessary for the marine plants employed as for animals, and its replacement in sea-water by ammonium, potassium, cæsium, lithium, magnesium, calcium, and strontium is injurious. The best substitutes are the elements which predominate in sea water, magnesium, calcium, and potassium.

The behaviour of various species indicates that each salt has a specific action.   N. H. J. M.

Antagonistic Action of Chemical Substances on Fungi. Chemical Preservation. THOMAS BOKORNY (*Cent. Bakt. Par.*, 1913, ii, 37, 168—267).—Numerous experiments are described on the action of various inorganic and organic substances on fungi, yeasts, etc. The results are summarised in tables.   N. H. J. M.

Assimilation of Nitrites by Moulds ALEXANDER KOSSOWICZ (*Chem. Zentr.*, 1913, i. 640 ; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, 2, 55—58).—Ten moulds have been found to subsist with nitrites as their source of nitrogen, and since in only two cases could ammonia be detected, the conclusion is drawn that the

nitrite ion is assimilated directly, without reduction. In good culture media, moderate concentrations of nitrites are not poisonous to moulds. J. C. W.

Decomposition of Carbamide, Uric Acid, Hippuric Acid, and Glycine by Moulds. II. ALEXANDER KOSSOWICZ (*Chem. Zentr.*, 1913, i, 640; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, 2, 51—55).—Several of the well-known moulds are able to make glycine or hippuric acid their sole source of nitrogen in presence of mannitol or dextrose, some of them producing ammonia. Certain moulds can depend on uric acid, hippuric acid, or glycine for their combined source of carbon and nitrogen. J. C. W.

Chemistry of the Higher Fungi. IX. Galls Produced by Exobasidium Vaccinii, Woron, on Rhododendron ferrugineum, L JULIUS ZELLNER (*Monatsh.*, 1913, 34, 311—319. Compare A., 1912, ii, 196).—The galls and the leaves on which they are found have been examined, and shown to contain the same constituents, the former containing a larger proportion of water-soluble substances, except tannin, and a smaller proportion of matter insoluble in water, than the leaves. On this and other grounds, it is suggested that the formation of galls on leaves is similar in character to the production and ripening of fruits.

The galls and the leaves were extracted in turn with light petroleum, ether, 95% alcohol and water, and the composition of these extracts was as follows: The galls yielded 1·71% to light petroleum; the product was a thick, semi-crystalline oil, having acid number 93·4, saponification number 165·1, and containing 12·5% of unsaponification matter, composed of (*a*) a *substance*, m. p. 129—130°, $[\alpha]_D^{18} - 29\cdot4°$, crystallising in colourless needles, and (*b*) a *substance*, m. p. above 280° (decomp.), much less soluble than the foregoing; both these products are phytosterols. The fatty acids of the oil are semi-solid. The leaves yielded 9·2% to light petroleum; the extract had acid number 60, saponification number 150, and contained the same two phytosterols as the gall extract, and also much resin and terpenes.

The ether extract of the galls amounted to 2·68%, and consisted of tannin and resin. The leaves yielded 8·34% to ether, and this extract also consisted of tannin and resin, the latter being somewhat different from that in the galls.

The alcohol extract of the galls amounted to 39·1%, and consisted of phlobaphen, dextrose, lævulose, tannin, and organic acids. The leaves yielded 32·6% to alcohol, and this extract consisted chiefly of tannin with some phlobaphen and a small amount of sugar.

The aqueous extract of the galls amounted to 13 32%; it contained some tannin, but was mostly gummy carbohydrate; no starch was present. The leaves gave only 1·7% of aqueous extract of similar composition to the foregoing, but containing some starch.

All the foregoing yields are expressed as percentages of the original material dried at 100°. T. A. H.

Chemistry of the Higher Fungi. X. JULIUS ZELLNER (*Monatsh.*, 1913, **34**, 321—336).—In this portion four fungi are dealt with, the method of investigation being the same as that described in the preceding abstract.

Armillaria mellea, Vahl.—The light petroleum extract was a semi-crystalline, thick, brown oil, having acid number 89·1, saponification number 179·6, iodine number 94·2, and containing notable amounts of lecithin and 4·5% of unsaponifiable matter, the latter consisting of a yellow resin and some ergosterol. The fatty acids were mostly liquid, but yielded when kept a mixture of crystalline acids, m. p. 62°, and acid number 210°. The ether extract contained some amorphous matter and ergosterol, m. p. 155°, $[a]_D - 114·8°$ in chloroform, which gave an acetyl derivative, m. p. 169°. No cerebrin was found. The alcoholic extract deposited after a time mannitol, m. p. 169—170° (possibly contaminated with mycose), dextrose, choline ?, and matter precipitated by lead acetate.

Lactarius piperatus, L. (compare Thörner, A., 1880, 44; Bissinger, A., 1884, 480; Chodat and Chuit, A., 1890, 80; Gérard, A., 1891, 606; and Bougault and Charaux, A., 1912, ii, 289).—The light petroleum extract amounted to 5·9%, and was a solid, yellow fat, having acid number 121·3 and saponification number 200·2. The unsaponifiable matter was separated into (1) a substance, m. p. 146—150°, probably a mixture of ergosterols; (2) a yellow resin; and (3) a sparingly soluble substance, m. p. 150° (approx. decomp.). This extract also contained lecithin. The fatty acids included some liquid acids, but the principal constituent was stearic acid, which was isolated in quantity (*loc. cit.*). The ether extract amounted to 1·2%, and consisted of yellow resin. The alcoholic extract contained mannitol (possibly contaminated with inositol), dextrose, and choline (compare Bourquelot, A., 1890, 103).

Pholiota squarrosa, Müll.—The light petroleum extract (3·8%) was a semi-solid, yellowish-brown fat, having acid number 51·8, saponification number 168·3, containing lecithin and 12·9% of unsaponifiable matter. From the latter a resin and a mixture of ergosterols, m. p. 159 (approx.), crystallising in colourless leaflets, were isolated. The ether extract resembled the foregoing in composition. The alcoholic extract contained mannitol, mycose, dextrose, choline, phlobaphen, and indefinite amorphous matter soluble in alcohol, but not in water.

Polyporus betulinus.—The light petroleum extract amounted to 3·5%, and had acid number 96·3, saponification number 155·0, iodine number 98·6, and contained 17·8% of unsaponifiable matter composed of a mixture of ergosterols, m. p. 139—144°, $[a]_D - 97·6°$, crystallising in needles or leaflets, cerebrin, resin, and gum. The ether extract was resinous, and contained a *substance*, $C_{31}H_{50}O_5$, m. p. 250° (approx. decomp.), which is probably an alcohol and is named *polyporol*. The alcoholic extract contained phlobaphen, mannitol, dextrose, traces of choline, and indefinite substances precipitated by lead acetate and other salts. The aqueous extract contained potassium phosphate and a carbohydrate, giving a pale

greyish-blue coloration with iodine, and readily hydrolysed by dilute hydrochloric acid. Winterstein's para*iso*dextran (A., 1895, i, 323) could not be obtained.   T. A. H.

Extraction of the Colouring Matter from the Cherry and Investigations of its Properties GIULIO MASONI (*Chem. Zentr.*, 1913, i, 546; from *Staz. sperim. agrar. ital.*, 1912, 45, 885—907).— The pigment may be extracted from fresh or dried cherries by means of water or alcohol with the help of a little tartaric or hydrochloric acid. The aqueous extract may be cleared by gelatin, and is violet-red and not very stable, whereas the alcoholic extract is clear, pure red in colour, and remains unaffected by heat or light. The dye may be applied to wool or food-stuffs. Its presence in wine may be detected, after clearing the liquid with lead acetate, by the addition of alum, when a violet coloration is produced, pure wines remaining colourless.   J. C. W.

Chemical Examination of Euphorbia pilulifera. FREDERICK B. POWER and HENRY BROWNING, jun. (*Pharm. J.*, 1913, [iv], 36, 506—510). —A complete chemical examination of the entire plant, collected in Fiji, has been made. None of the definite constituents isolated has any specific physiological action, so that such therapeutical value as the plant possesses cannot depend on any single definite substance. An alcoholic extract of the plant was steam-distilled, and yielded (1) a volatile oil, b. p. 235—260°, giving the colour reaction of furfuraldehyde; (2) a portion soluble in water; (3) a resinous portion, insoluble in water; the two latter portions of the extract were then examined by methods which are described in detail, and gave the following products:

Portion Soluble in Water.—This yielded gallic acid, quercetin, a small amount of jambulol (see also below), and a phenolic *substance*, $C_{25}H_{18}O_5$, which crystallised in microscopic clusters of needles, and decomposed, but did not melt, at 340°. There was also present a lævorotatory sugar, which yielded *d*-phenylglucosazone, some amorphous glucosidic matter, traces of an alkaloidal substance, together with indefinite oily and extractive matters.

Portion Insoluble in Water.—This yielded melissic acid, ceryl alcohol, triacontane, a *phytosterol*, m. p. 132—133°, crystallising in flattened needles, and giving an *acetyl* derivative, m. p. 122—123°; a *phytosterolin*, $C_{33}H_{56}O_6$(?), m. p. 297° (decomp.), crystallising in colourless needles, and yielding an *acetyl* derivative, m. p. 161—162°, crystallising in flattened needles; jambulol (T., 1911, 99, 962, and A., 1912, ii, 480), and a mixture of palmitic, oleic, and linoleic acids. In addition, a monohydric alcohol, *euphosterol*, $C_{25}H_{39}\cdot OH$, m. p. 274—275°, was obtained. This crystallises from petroleum in needles, gives the colour reaction characteristic of this class of substances (T., 1909, 95, 739; 1912, 101, 2425), and is optically inactive. It yields an *acetyl* derivative, m. p. 295—297°, $[\alpha]_D + 8\cdot2°$ in chloroform, and this on bromination in cold chloroform gives *bromoacetyleuphosterol*, m. p. 183—186°, crystallising in small needles from a mixture of alcohol and ethyl acetate.

Euphosterol is probably accompanied by other alcohols of the same series, since in recrystallising the acetyl derivative two other fractions, m. p. 205—210° and m. p. 230—260°, were obtained.

T. A. H.

Causes of the Natural Changes in the Latex of Hevea Brasiliensis. G. STAFFORD WHITBY (*Z-itsch. Chem. Ind. Kolloide*, 1913, 12, 147—157).—Experiments are described which have been made in order to ascertain the nature of the changes which are involved in the coagulation of the latex of *Hevea Brasiliensis* when this is left in contact with the air. The observations indicate that coagulation is brought about by an enzyme (probably a protease). Anærobic decomposition occurs in those portions which are out of contact with the air, and evidence has also been obtained which indicates the presence of an oxydase, to which the name, *hevease*, is applied.

A fourth factor in the coagulation process consists in ærobic decomposition, which occurs in the later stages, and gives rise to an alkaline mucus which causes the latex to become milky. The relative importance of these four independent processes depends very largely on the conditions under which coagulation of the latex occurs.

H. M. D.

Herbage Studies II. Variation in Lotus Corniculatus and Trifolium repens (Cyanophoric Plants). HENRY E. ARMSTRONG, E. FRANKLAND ARMSTRONG, and EDWARD HORTON (*Proc. Roy. Soc.*, 1913, *B*, 86, 262—269).—It is established that in addition to the common widely distributed cyanophoric form of *Lotus corniculatus*, a botanically indistinguishable form exists, in which the power of producing the cyanophoric glucoside is all but suppressed. *Lotus major* is uniformly cyanophoric. The normal form of *L. corniculatus* contains both glucoside and the correlated enzyme; a second form is rich in enzyme, but contains mere traces of the glucoside, whilst in the third form the amount of both glucoside and enzyme is very small.

The conclusion is drawn that the above differences are due to the presence or absence of definite factors rather than the consequence of the operation of special conditions of environment.

Whereas cultivated white clover (*Trifolium repens*) is without cyanide, wild white clover always contains a cyanophoric glucoside.

The determination of the enzymic activity of a number of specimens of *Trifolium repens* showed that all were moderately active towards salicin, but that the cultivated variety alone was practically without action on linamarin and prunasin.

The bearing of the chemical peculiarities of the two types of clover on their value as food materials is discussed.   E. F. A.

Chemistry of Peat Moss (Sphagna). JOSEF IBELE (*Ber. deut. bot. Ges.*, 1913, 31, 74—77).—When *Sphagnum papillosum* is oxidised with hydrogen peroxide a substance soluble in sodium hydroxide

solution is obtained, which becomes insoluble when precipitated with acid and dried. Formic acid and ammonia are also formed.

Sphagnum dissolves almost completely in hydrochloric acid containing antimony trichloride. Ammonia is liberated, but no methylamine could be detected.   N. H. J. M.

Glucosides and Oils of the Primrose. A. GORIS, M. MASCRÉ, and CH VISCHNIAC (*Chem. Zentr.*, 1913, i, 310—311; from *Bull. Sci. Pharmacol.*, 1912, 19, 577—598, 648—670; *Wiss. ind. Ber. Roure-Bertrand fils*, 1912, 6, 3—73 Compare A., 1910, ii, 63).—The crude glucosides which form about one part per thousand of the roots of *Primula officinalis* may be separated by fractionation from a mixture of ethyl acetate and alcohol. Primverin (I), $C_{20}H_{28}O_{13}$, m. p. 206° (corr.), $[\alpha]_D -71°53'$, yields on hydrolysis with dilute acids, *methyl β-methoxyresorcylate*, $C_9H_{10}O_4$, m. p. 49°, which develops a violet-red colour with ferric chloride, and two molecular proportions of monoses. The enzyme primverase, however, produces the biose, *primverose*, $C_{11}H_{20}O_{10}$, m. p. 209—210°, which exhibits multirotation; $[\alpha]_D +23°1'$, $-2°3'$ after twenty-four hours (1·846 grams in 75 c.c. H_2O), $+23°11'$, $-3°17'$ after twenty-four hours (1·35 grams in 26 c.c. of water). It reduces Fehling's solution (0·0673 gram = 77 mg. Cu), forms an *osazone* in light yellow needles, m. p. 204—207°, and contains a pentose, apparently in combination with a hexose.

$$CO_2Me$$
$$\cdot O \cdot C_{11}H_{19}O_9$$

$$OMe$$
(I.)
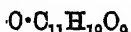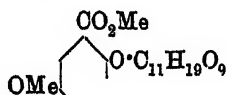
$$CO_2Me$$
$$OMe \quad O \cdot C_{11}H_{19}O_9$$
(II.)

Primulaverin, $C_{20}H_{28}O_{13},2H_2O$, m. p. 163° (corr.), $[\alpha]_D -66°65'$, yields on hydrolysis the same sugars and *methyl m-methoxysalicylate*, mixed with methyl β-methoxyresorcylate. It has not yet been obtained pure, but the true primulaverin would have the formula II.

The ethereal oils of the primrose root contain the above esters, whilst the oil from the flowers contains, in addition, over 10% of an unhydrolysable substance.   J. C. W.

Willow Bark. I. GEORGEI GEORGEVITSCH POVARNIN and A. BABABANOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 267—271).—The authors have examined the barks of a number of willows, including hybrids, with the object of classifying them according to their chemical reactions. Tannides of two distinct types occur in the barks (see following abstract).   T. H. P.

Willow Bark. II. GEORGEI G. POVARNIN and N. SHURAVLEV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 271—283. Compare preceding abstract).—The bark of the hybrid willow, *Salix alba × S. viminalis*, contains, in addition to phlobaphens, two tannides which are char-

acterised by their reactions with ferric chloride and with ammoniacal copper sulphate. The tannide of *S. alba* is a tannoside, and may be separated from that of *S. viminalis,* which contains free sugar, by its different solubility in a mixture of methyl alcohol and ether. The former gives anhydro- and oxy-phlobaphens, and it contains protocatechuic acid, whilst the tannide of *S. viminalis* contains pyrogallol, but the principal decomposition products are phlobaphen and sugar.   T. H. P.

Manuring of Cultivated Plants by means of Carbon Dioxide. ADOLPH HANSEN (*Chem. Zentr.*, 1912, ii, 2135; from *Naturw. Rundsch.*, 1912, **27**, 547—550).—It was noticed that the vegetation in the neighbourhood of a natural carbonic acid spring was particularly fine, and the administration of carbon dioxide to cultivated plants is found to increase the dry weight considerably. It is suggested that the gas is loosely combined with the chlorophyll in the same way as oxygen is united to the pigment of the blood.
                                                                J. C. W.

Importance of the Potassium in Felspar for Plants. EDWIN BLANCK (*J. Landw.*, 1913, **61**, 1—10. Compare *ibid.*, 1912, **60**, 97).—Pot experiments in which oats were manured with various potassium minerals. Previous results, indicating that the tubes are more suitable as sources of potassium for plants, are confirmed.
Plagioclase gave much better results than microlin and orthoclase, which were almost without effect.   N. H. J. M.

History of Maize Sugar. PH. DE VILMORIN and FERDINAND LEVALLOIS (*Bull. Soc. chim.*, 1913, [iv], **13**, 294—301) —The authors give an extensive review of the efforts which have been made to extract a crystallisable sugar from maize on the industrial scale, special reference being made to the work of Pallas and to the recent investigations of Stewart and of Heckel (*Compt. rend.*, 1912, **155**, 686).
A series of experiments have been made on maize from Verrières and from Antibes, the conditions, however, being rather unfavourable. In these circumstances, the juice from maize from which the ears had been removed during growth was found to contain 10% of sucrose, whilst a greater proportion could be extracted from sugar maize. From the industrial point of view, the extreme rapidity, both of formation and of decomposition of sugar in maize, constitutes a serious difficulty, which, however, could possibly be obviated to some extent by the systematic employment of different varieties of maize.   H. W.

Respiration and Metabolism in Ruminants. NATHAN ZUNTZ, RICHARD VON DER HEIDE, KLEIN, I. VON MARKOFF, FÜRST VON DSCHANDIERI, and DJADKOW (*Landw. Versuchs-Stat.*, 1913, **79**-**80**, 781—814).—The utilisation of foods by cattle varies according to the mechanical condition of the mixture, and the same food will give different results when given in conjunction with other foods. An experiment is described in which potatoes were compared with

the corresponding amount of potato slump to which starch was added to replace that which had been lost; whilst malt and yeast were added to the potatoes. Although the two foods had practically the same composition, the results with starch were essentially different from those with potatoes. When starch is given in conjunction with hay, the crude fibre, protein, and fat are digested in diminished amounts. In the case of the non-nitrogenous extract the amount in the fæces was diminished by the starch. This does not, however, indicate better resorption, as there is no doubt that the extractive substances were lost by fermentation. The comparison of food and fæces is misleading in the case of ruminants.

It is desirable in feeding experiments to estimate the amount of oxygen utilised as well as the amounts of respired nitrogen and carbon dioxide. A method for estimating the oxygen is described.

The various estimations in respiration experiments should be made at short intervals.

Methods for investigating the fermentation processes of the rumen are discussed.   N. H. J. M.

Employment of Dialysis in the Estimation of the Oxidising Power of Soils. JOSEF KÖNIG, JULIUS HASENBAUMER, and K. GLENK (*Landw. Versuchs-Stat*, 1913, **79–80**, 491—539).—Several soils were subjected to dialysis, and the amounts of organic matter, calcium, magnesium, potassium, phosphoric acid, and sulphuric acid in the solutions estimated. It was found that soils which were heated at 150° yielded considerably more soluble matter than soils which had not been heated; similar results, but less marked, were obtained with soils dried, under reduced pressure, at 95—98°. Clearer indications of the changes which soils undergo when heated, and even when air-dried, were obtained by estimating the electrolytic conductivity. The results indicate that in the ordinary drying of soils the colloidal state is in part destroyed.

The amounts of carbon dioxide produced in six different soils, and in the same soils with small amounts of dextrose and urea respectively, were estimated daily for three weeks; and at the end of the experiment the amounts of ammonia and nitrates and the numbers of bacteria were estimated (compare Hutchinson and Marr, A., 1911, ii, 430). As regards nitrification, the urea was almost completely nitrified in the loamy soil, whilst the clay soil showed very slight nitrification. Addition of dextrose considerably increased the number of bacteria in all the soils. Electrolytic conductivity was increased by urea and diminished by dextrose.

The results of pot experiments with oats showed that heating the soil at 95—98° in a vacuum increased both the total growth and the mineral constituents. Addition of dextrose and gum arabic to loamy sand and loam diminished the yield of grain and straw.

                                                    N. H. J. M.

Colloidal Substances in Soil Solutions. Production of Soda in Soils. Alkali and Salt Soils. K. K. GEDROIZ (*Bied. Zentr.*, 1913, **42**, 76—79; from *J. exper. Landw.*, 1912, **13**, 421).— The amount of colloids in soil extracts (except alkali soil extracts)

was found to vary from 0·0018 to 0·0200%, and in Russian arable soils from 0·0058 to 0·0147%. The dry matter dissolved by water amounted to 0·0385 to 0·0591%. The coagulation of such small amounts of colloidal substances can have very little effect on the physical properties of the soils; and the changes brought about by frost, electrolytes, and liming, etc., are attributed to their influence on substances mechanically suspended in the soils, especially the gels.

In the case of alkali soils the total colloids, mineral and organic, varied from 0·0990 to 0·4494%; in such soils coagulation of the colloids may influence the physical properties of the soil.

In typical alkali soils, nearly free from chlorides and sulphates, the amount of soda in successive extracts decreases much more slowly than would be the case if only pre-existing soda were dissolved. In alkali soils containing much sodium chloride, but little sulphate, alkalinity begins only after some of the chloride is washed out.

A loamy, black soil, treated with sodium chloride and calcium carbonate, failed to yield appreciable amounts of soda, and only small amounts were produced by treatment with sodium sulphate and calcium carbonate. Under the combined influence of sodium chloride and sulphate, alkaline, dark-coloured solutions were obtained after the removal of most of the chloride and sulphate; in presence of calcium carbonate the soil yielded soda. The conclusion is drawn that the soda is produced from zeolites. The production of soda is hindered by excessive amounts of sodium chloride and sulphate.   N. H. J. M.

The Fertilising Action of Sulphur. A. DEMOLON (*Compt. rend.*, 1913, **156**, 725—728).—Further experiments with sulphur (compare A., 1912, ii, 382) show that it can act as a useful addition to farmyard manure as a fertiliser, but that its action diminishes and vanishes in the presence of a large amount of organic and mineral fertilisers. Potatoes benefit most by the addition of sulphur. On light lands it has an injurious effect on cereals. Addition of sulphur in amount equal to the nitrogen supplied has given the same results as a complete mineral fertiliser. The fertilising action of the sulphur is due (*a*) to its action on the soil bacteria, (*b*) to its progressive transformation into sulphuric acid.   W. G.

[Manurial] Action of Different Forms of Nitrogen. W. SCHNEIDEWIND (*Bied. Zentr.*, 1913, **42**, 101—110; from *Arb. deut. Landw.-ges.*, Heft. 217).—Pot and field experiments on the action of sodium and calcium nitrates, calcium nitrite, ammonium salts, calcium cyanamide, and urine. On the whole the best results were obtained with sodium and calcium nitrates. Ammonium salts were not regular in their action; in one case, both on dry and wet soils, ammonium salts gave better results than nitrate. Both with oats and potatoes, nitrates and ammonium salts gave the same results. Calcium cyanamide acted most favourably when applied in the autumn for winter cereals. Urine was unsatisfactory both on light and loamy soils. The effect of calcium nitrite was variable.

The application of large amounts of manure to light soils in the autumn is useless; ammonium salts and calcium cyanamide may, however, be applied to soils of better quality.   N. H. J. M.

Influence of Ammonium Sulphate on the Phosphate Manuring of Oats. EILHARD A. MITSCHERLICH and W. SIMMERMACHER (*Landw. Versuchs-Stat.*, 1913, 79–80, 71—96).—Addition of ammonium, sodium, and magnesium sulphates considerably increased the solubility of the phosphoric acid of di- and tri-calcium phosphates, whilst in presence of calcium phosphate the solubility is diminished.

The results of vegetation experiments, in which oats were manured with di- and tri-calcium phosphates, showed that the addition of small amounts of ammonium sulphate increased the amounts of phosphoric acid assimilated even in presence of considerable amounts of soluble salts which would be acting in the same direction.

In the case of superphosphate and basic slag, addition of ammonium sulphate was without effect on the assimilation of the phosphoric acid by oats.   N. H. J. M.

Manuring with Sodium Salts. BERNHARD SCHULZE (*Landw. Versuchs-Stat.*, 1913, 79–80, 431—448). — Sodium is utilised by plants, and may take the place of potassium to a certain extent. The sodium of sodium chloride is taken up by plants with great rapidity; and, as it is not absorbed by soils to the same extent as potassium, its manurial action lasts longer if not washed out of the soil.

Whilst potassium salts decompose sodium zeolites in the soil, sodium salts have a very slight action, if any at all, on potassium zeolites.   N. H. J. M.

Lime Rich in Silica as Manure. HEINRICH IMMENDORFF (*Landw. Versuchs-Stat.*, 1913, 79–80, 891—901).—Different soils were rubbed in a mortar with lime and water, and then put on to glass plates to dry in order to ascertain whether any hardening of the soil takes place owing to the presence of silica. The limes employed contained from 0·03 to 19·51% of soluble silica (Portland cement). The same soils were treated with water alone for comparison.

The results showed that no hardening of the soil takes place when lime containing large amounts of soluble silica are employed. Hydrated silica may itself have a favourable effect on the soil by increasing its absorptive power.   N. H. J. M.

Organic Chemistry.

Composition of Mineral Oils of High Boiling Point. I. The Viscous Components of Mineral Oils of High Boiling Point. JULIUS MARCUSSON (*Chem. Zeit.*, 1913, **37**, 533—534).—Previous .investigations (*ibid.*, 1911, **35**, 729) have shown that the more viscous portion of mineral oils (naphthenes, polynaphthenes, paraffins, and olefines) is that which does not react with formaldehyde and sulphuric acid, whilst the reacting portion (benzene derivatives, unsaturated naphthenes, and terpenes) is comparatively mobile. Paraffins have small viscosity, whilst that of naphthenes is greater than that of paraffins of the same molecular weight. The viscosity of mineral oils cannot therefore be attributed to the presence of paraffins. This is confirmed by the fact that the viscosity of lubricating oils can be raised by removal of solid paraffins and lowered by their addition. Olefines are present in too small amount to exert a distinct effect on the viscosity, so that the diminution in viscosity effected by treating oils with fuming nitric acid at $-10°$ must be attributed to the destruction of polynaphthenes. The viscosity must therefore be due to the presence of naphthenes and polynaphthenes. The former are mainly present in the portions distilling below $300°$, so that in oils of high b. p. and high viscosity, the chief saturated hydrocarbons are polynaphthenes. This is confirmed by analysis of a heavy Russian machine oil, which, before purification, contained $C = 85.79\%$ and $H = 12.78\%$, whilst after treatment with formaldehyde and sulphuric acid, the figures obtained were $C = 85.41\%$, $H = 13.07\%$, which correspond with the results to be expected from a mixture of condensed naphthenes. Further confirmation is found in the high molecular weight of machine oils, which ranges from 300 to 400 with a mean value of about 350, corresponding with compounds containing twenty-five atoms of carbon in the molecule.

Highly viscous oxygen compounds are present in nearly all machine oils, but, generally, in such small amount that their effect is inconsiderable.

The present communication deals only with machine oils. Cylinder oils are under investigation. H. W.

Composition of Mineral Oils of High Boiling Point. II. Components of Liquid Paraffin and their Behaviour towards Aluminium Chloride. JULIUS MARCUSSON and C. VIELITZ (*Chem. Zeit.*, 1913, **37**, 550—553).—The so-called liquid paraffin is generally regarded as a mixture of liquid hydrocarbons of the paraffin series. This view, however, appears improbable, since the substance is usually obtained from Russian oils which are comparatively poor in such hydrocarbons.

Two specimens of liquid paraffin were employed, having D_4^{20} 0.8827, 0.8858, n^{20} 1.4797, 1.4799, specific viscosity at $20°$, 23.0, 29.9,

$[\alpha]_D$ +2·13, 2·35, respectively. The density and refractive index indicate that hydrocarbons of the paraffin series cannot be the main components of the mixture, whilst ultimate analysis points to the presence of polynaphthenes.

In order to decide whether the optical activity is attributable to *iso*paraffins or polynaphthenes, a specimen of liquid paraffin was fractionated under greatly reduced pressure. Density, viscosity, refractive index, and optical activity were found to increase with increasing b. p. of the fraction. Since the fraction, b. p. 255—277°/ 4 mm., was completely liquid and only yielded a trace of precipitate when cooled with alcohol–ether to −20°, it appears improbable that *iso*paraffins can be the cause of activity. This is confirmed by the results of an ultimate analysis, and further by the fact that optical activity is not lost when liquid paraffin is subjected to energetic treatment with fuming nitric acid. Activity must therefore be due to the presence of polynaphthenes, which is in accord with the observation of Bushong and Humphrey (*Chem. Zeit.*, 1912, **36**, 1139) that optically active naphthenic acids are present in mineral oil.

The optically active constituents of liquid paraffin are stable towards fuming sulphuric or fuming nitric acid, but are readily inactivated by aluminium chloride. When a solution of liquid paraffin in carbon disulphide was heated on the water-bath during three hours with aluminium chloride and the residue left after removal of the solvent was extracted with light petroleum, a colourless oil was obtained, which possessed feeble optical activity and considerably lower density, refractive index, and viscosity than the original material. From that portion of the reaction product which was insoluble in light petroleum, a viscous, brown substance was obtained, solutions of which were too deeply coloured to permit polarimetric observation. In the absence of any solvent, similar inactivation was observed. With light petroleum as solvent, however, the recovered oil had nearly the same properties as the original specimen. This difference is probably attributable to the fact that the yellowish-white additive product formed from liquid paraffin and aluminium chloride is practically insoluble in light petroleum, whilst it is appreciably soluble in carbon disulphide and also in liquid paraffin. In the first case, therefore, the liquid paraffin becomes practically protected from further action of aluminium chloride.

Finally, a series of experiments has been performed on the action of aluminium chloride on different optically active substances dissolved in carbon disulphide. Camphor and castor oil were not affected. Rosin oil, oil of turpentine, cholesterol, and the unsaponifiable portions of wool grease yielded black masses from which optically inactive products were extracted by light petroleum.   H. W.

Structure of Acetylene. ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, **17**, 320—321. Compare this vol, ii, 494).—The total number of valencies in acetylene calculated from the critical data by the author's formula is ten. The formula of acetylene at its critical point is therefore H—C≡C—H, and not C≡C≡H₂.   R. J. C.

Preparation of βγ-Dihalogen isoPentanes by the Chlorination of β-Halogen isoPentane. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 257600).—When the vapours of monohalogenated tertiary isopentanes are treated with chlorine (or bromine), they readily furnish a satisfactory yield of the technically important βγ-dihalogen isopentanes, and the preparation of βγ-dichloroisopentane, b. p. 60°/60 mm., from β-chloroisopentane is described. F. M. G. M.

The Preparation of Carbon Tetraiodide. MARCEL LANTENOIS (Compt. rend., 1913, 156, 1385—1387).—A critical study of the various methods recommended for the preparation of carbon tetraiodide (compare Spindler, A., 1886, 434; Moissan, A., 1891, 1420; Robineau and Rollin, A., 1895, i, 123). The author adopts Spindler's method, but prefers to replace the calcium iodide with lithium iodide, which gives a very pure product on heating it with excess of carbon tetrachloride in a vacuum in a sealed tube at 90—92° for five days. The best solvents for carbon tetraiodide are benzene, acetone, and carbon disulphide. W. G.

Higher Tertiary Alcohols Derived from Palmitic and Stearic Esters. HUGH RYAN and THOMAS DILLON (Proc. Roy. Irish Acad., 1912, B, 29, 235—245).—A series of tertiary alcohols has been prepared by the action of Grignard's reagents on esters of palmitic and stearic acid. The latter were readily obtained by the addition of a few c.c. of concentrated sulphuric acid to a hot solution of the acid in excess of the requisite alcohol, the yields in every case being more than 90% of the quantity theoretically obtainable. The following esters were obtained in this manner: methyl palmitate, needles, m. p. 28°; ethyl palmitate, long needles, m. p. 24·2°; n-propyl palmitate, needles, m. p. 18·8—19·2°; methyl stearate, needles, m. p. 38°; ethyl stearate, needles, m. p. 31°; n-propyl stearate, prisms, m. p. 28·6°.

For the preparation of tertiary alcohols, the solid ester was added in small portions to an ethereal solution of the necessary Grignard's reagent. There were thus obtained: dimethylpentadecylcarbinol, $C_{18}H_{38}O$, needles, m. p. 35°; diethylpentadecylcarbinol, curved needles, m. p. 34—35°; diphenylpentadecylcarbinol, prisms, m. p. 47—48°; dimethylheptadecylcarbinol, needles, m. p. 44—45°; diethylheptadecylcarbinol, needles, m. p. 44—45°; dipropylheptadecylcarbinol, needles, m. p. 28—30°; diphenylheptadecylcarbinol, long, curved needles, m. p. 58°. The action of an ethereal solution of magnesium naphthyl bromide on methyl stearate led to the formation of naphthyl heptadecyl ketone, $C_{17}H_{35}·CO·C_{10}H_7$, m. p. 55°.

Diethylheptadecylcarbinyl acetate was obtained as an oily liquid, which solidified when placed in iced water, by the action of acetyl chloride on diethylheptadecylcarbinol.

Dimethylpentadecylcarbinol, when heated on the sand-bath with sodium acetate and acetic anhydride, yielded a mixture of the corresponding acetate and unsaturated hydrocarbon. A similar result was obtained with diethylheptadecylcarbinol.

Dimethylheptadecylcarbinol was apparently not affected when heated with potash-lime at 250°. At 300°, however, unsaturated substances

were produced, but no evolution of hydrogen was observed. Diphenyl-heptadecylcarbinol similarly yielded unsaturated substances at 300°.

H. W.

Basic Properties of Oxygen. II. OTTO MAASS and DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1913, **35**, 535—543).—In an earlier paper (A., 1912, i, 825) it has been shown that the compounds formed by the union of halogens or halogen hydrides with organic substances containing oxygen differ in many respects from molecular aggregates containing water or alcohol of crystallisation. In order to ascertain whether such compounds exist in solution, conductivity determinations have been made of the two-component systems of hydrochloric acid with ethyl and methyl ethers and with ethyl and methyl alcohols over the complete concentration range at −89°. The results are compared with the freezing-point curves of the different systems. In the case of methyl ether, two compounds are formed, namely, Me_2O,HCl and $Me_2O,4HCl$ (?). With ethyl ether, three compounds are produced: Et_2O,HCl, m. p. −92°; $Et_2O,2HCl$, m. p. −88°; and $Et_2O,5HCl$, m. p. −89°. Methyl and ethyl alcohols each yield only one compound, namely, $MeOH,HCl$, m. p. −62°, and $EtOH,HCl$, m. p. −65°. The conductivity curves indicate the probability of the existence of compounds in solution.

E. G.

A Derivative of Quinquevalent Tungsten. ARTHUR FISCHER and LOUIS MICHIELS (*Zeitsch. anorg. Chem.*, 1913, **81**, 102—115. Compare this vol., ii, 513).—The electrolysis of a solution of tungsten hexachloride in absolute alcohol gives at the platinum cathode a green, crystalline compound, $C_6H_{16}O_3Cl_2W$. It is decomposed by hot alcohol, but may be recrystallised from a mixture of alcohol and chloroform at 60°, cooling in ice. The compound forms bright green leaflets, with metallic lustre and slight fluorescence. It is slowly decomposed by hot water, yields the blue oxide when strongly heated, and gives the iodoform reaction. More than two-thirds of the carbon is evolved on heating in the form of ethylene. Oxidation with permanganate indicates that the tungsten is quinquevalent. The reactions indicate the composition $WCl_2(OEt)_3$, but the molecular weight is double this, and the exact constitution is uncertain.

C. H. D.

Catalytic Actions of Colloidal Metals of the Platinum Group. IX. The Hydrogenation of Egg-lecithin. CARL PAAL and HERMANN OEHME (*Ber.*, 1913, **46**, 1297—1304).—As in previous experiments with certain fats (A., 1908, i, 599; 1909, i, 358), so also it has been found possible to reduce egg-lecithin to a crystalline substance. Merck's reddish-brown, wax-like egg-lecithin had the iodine value, 55·3, but the volume of hydrogen absorbed in presence of colloidal palladium in 90% alcoholic solution was higher than this value would predict, being about 59 c.c. instead of 48·4 c.c. per 1 gram. The *hydrolecithin* partly separates from the solution, and may be recrystallised from chloroform and acetone as a white powder which sinters at 83—84°. On hydrolysis with barium hydroxide, it gave glycerol, phosphoric acid, and choline, which was identified as the

aurichloride, whilst the fatty acids recovered from the soap were found, after fractional crystallisation, to contain chiefly stearic acid, which would arise from the unsaturated C_{18}-acids of egg-lecithin. The presence of small quantities of acids of lower molecular weight, probably myristic, decoic, or lauric acids, showed that the substance and consequently the starting material were not quite homogeneous. Egg-lecithin is, however, chiefly a palmityl-linolyl-lecithin, and the analysis of the hydrolecithin agreed fairly well with $C_{42}H_{86}O_9NP$, the formula of a palmityl-stearyl-lecithin. J. C. W.

Uranyl Formate. GASTON COURTOIS (*Bull. Soc. chim.*, 1913, [iv], 13, 449—454).—The properties of *uranyl formate*, $(HCO)_2UO_2,H_2O$, which is obtained in non-deliquescent, yellow octahedra by digesting the hydrated oxide, UO_3,H_2O, with dilute formic acid at 80°, are very different in many respects from those described by Œchsner de Coninck and Raynaud (this vol., i, 333). When crystallised from ice water, it still contains $1H_2O$, and it is not dehydrated by prolonged sojourn in a vacuum desiccator. When dried in this manner, it is stable up to 100°, loses water at 150°, but also formic acid. A moist sample loses water and formic acid at 100°, and becomes insoluble. The solubilities are 7·2% in water at 15°, 4·9% in methyl alcohol at 18°, only slightly soluble in concentrated formic acid or alcohol, insoluble in other organic media.

The concentrated solution slowly deposits a *basic* salt in the cold and dark, quickly on boiling, in the form of yellowish-white, truncated prisms of the composition $(HCO)_2UO_2,H_2O$, $UO_3,2H_2O$. Prolonged boiling with water results in the acid, UO_3,H_2O. When exposed to light for some time, dilute solutions of the formate gradually deposit this basic salt mixed with a small amount of a violet hydrate of uranoso-uranic oxide. Even in methyl alcohol no brown uranium oxide was obtained, but the above violet substance, which was transformed into the pale yellow oxide, $UO_3,2H_2O$, in the air, and into the yellowish-white acid, UO_3,H_2O, on boiling with water.

J. C. W.

Molecular Association of Acetic Acid. ÉMILE BAUD (*Bull. Soc. chim.*, 1913, [iv], 13, 435—438).—According to the surface tension measurements of Ramsay and Shields (A., 1894, ii, 179), acetic acid exists in double molecules at the ordinary temperature. This was found to be the case when the acid is mixed with some organic solvents (A., 1912, ii, 233, 331, 1147), and is again confirmed by cryoscopic measurements in nitro- and chloro-benzene. The fact holds good even for strong solutions, from which it follows that the pure acid is bimolecular, and that the solvent has no associating influence in these cases.

Formic acid, however, like water, has a dissociating effect and the unimolecular value is obtained. The freezing-point curve for mixtures of the two acids does not indicate the formation of a compound, but it is assumed that combination does take place, since the heat absorbed on mixing the two substances is much less than the heat of dissociation of the double molecules. [An equilibrium between the double molecules

and the mixed molecules, $(C_2H_4O_2)_2 + (CH_2O_2)_2 \rightleftharpoons 2(C_2H_4O_2,CH_2O_2)$, would require that in a dilute solution of acetic acid in formic acid, the acetic acid molecule would produce two molecules of the mixed acid and cause an excessive depression of the freezing point, leading, therefore, to the unimolecular value for the molecular weight.

J. C. W.

Margaric Acid and its Relations to Palmitic and Stearic Acids. ROBERT F. RUTTAN (*8th Inter. Cong. Appl. Chem.*, 1912, **25**, 431—442).—The history of margaric acid is related, a method of preparing the acid by the Grignard reaction is described, and the chief constants of the acid are recorded in comparison with those of palmitic and stearic acids.

When cetyl iodide is treated with magnesium in ether, in presence of iodine as a catalyst, micaceous crystals of the organo-magnesium compound separate. If the mixture is then treated with carbon dioxide, a mixture of ditriacontane and margaric acid is formed, the yield of the acid being 50% of the theoretical under the best conditions, which include the use of dry reagents throughout the operations. A method for the separation of the hydrocarbon and acid is described. Margaric acid crystallises in colourless, bulky, shining plates, melts at 59·9—60° (corr.), and solidifies at 58·8°. It has D 0·8532 at its melting point, $n = 1·4342$ at 60°, and the coefficient of expansion is $6·65 \times 10^{-4}$ at 60—80°. The following quantities (grams) dissolve in 100 grams of dry alcohol at the temperatures named : 0°, 1·53 ; 5·4°, 2·42 ; 10°, 4·12 ; 15°, 6·72 ; 21°, 13·4 ; 28°, 32·14. Methyl margarate, m. p. 29°, forms waxy scales. Ethyl margarate, m. p. 27·5°, crystallises in waxy plates. *Ethylene margarohydrin*, m. p. 53·2°, forms pearly scales, and *ethylene dimargarate*, m. p. 70·4°, glistening plates.

T. A. H.

Saponification of Triglycerides. JULIUS MEYER (*Chem. Zeit.*, 1913, **37**, 541—542).—The author criticises the experiments of Fortini (A., 1912, i, 826) on the saponification of triolein with alkali hydroxide in alcohol. The latter found that the curves obtained by plotting (1) quantity of triglyceride hydrolysed against time, or (2) acetyl number against time, were composed of three parts corresponding with (*a*) formation of diglyceride ; (*b*) formation of monoglyceride, and (*c*) formation of free fatty acid.

According to the author, the amount of alkali consumed is not a measure of the quantity of triglyceride saponified, since a portion of it is used in decomposing di- and mono-glycerides (compare Kellner, A., 1909, i, 357, 548, 759). Also, by plotting alkali consumed against time, a continuous curve is obtained in the saponification of triacetin in homogeneous solution by 0·01 and 0·02N potassium hydroxide (Meyer, A., 1909, ii, 803). Further, the determination of the acetyl number after definite intervals of time is not a satisfactory method of following the course of the reaction, since, particularly with the unsaturated oleic acid and its glycerides, this number depends greatly on the conditions under which the determination is executed, and is further complicated by the decomposition of the triglyceride into olein

acetate and glycerol occurring with intermediate formation of di- and mono-glycerides (compare Kremann, A., 1905, ii, 630; 1908, i, 120; Fanto and Stritar, 1908, i, 499).　　　　H. W.

The Behaviour of Paints Under the Conditions of Practice, with Special Reference to the Aspersions Cast on Lead Paints. HENRY E. ARMSTRONG and C. A KLEIN (*J. Soc. Chem. Ind.*, 1913, **32**, 320—331).—This communication is, to a great extent, critical and polemical against the work of Baly (*The Oil and Colour Trades Journal*, 1911, 1518; A., 1912, i, 533), and the report of Breton in connexion with lead paints. The experimental part deals with the formation of volatile products from linseed and other oils and the ordinary materials used in making paints, and with the test for lead in the volatile products, if any, from paint materials. The leaf of the common shrub, *Aucuba Japonica*, or the spotted Japanese laurel, is used as a test for volatile products, in the presence of which it blackens more or less rapidly.

The conclusions arrived at are: The vapours produced during the drying of white-lead pastes and paints do not contain lead. The vapours given off as paints dry consist of turpentine for the most part, together with oxidation products of the oil; the latter are common to paints generally containing oil so treated that it will dry. The oxidation products formed from the oil during drying are harmless under the conditions of practice. The toxic effects sometimes experienced from drying paints are to be ascribed to turpentine; in many cases effects which have been regarded as due to lead-poisoning are attributable to other causes, especially to turpentine. The dangers attending the use of lead compounds are only the well-known mechanical dangers.　　　　T. S. P.

Cerebronic Acid. II. PHŒBUS A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1913, **14**, 257—266. Compare A., 1912, i, 936).— Previous work indicated that cerebronic acid has the structure of an α-hydroxypentacosoic acid; on reduction the acid formed a hydrocarbon, m. p. 54—57°. According to Krafft and Marie, *n*-pentacosane has m. p. 53·5—54°. The experiments were repeated with a larger supply of material, and the melting point came out at the latter figure. By reduction of the acid, $C_{24}H_{48}O_3$, obtained by oxidation of cerebronic acid, a hydrocarbon, melting at 51—52°, was obtained, which is the melting point of normal tetracosane. Cerebronic acid is a α-hydroxy-*n*-pentacosoic acid.

Acetylcerebronic acid, $C_{25}H_{49}O_3$, obtained by the action of acetic anhydride on cerebronic acid, is a white, crystalline solid, m. p. 55·5—56°, and solidifies at 53—54°.　　　　W. D. H.

Formation of β-Ketone Esters by the Application of Reformatsky's Reaction. TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1913, **35**, 582—585).—Fittig and Daimler (A., 1887, 361) have shown that ethyl chloroacetate reacts with ethyl oxalate in presence of amalgamated zinc with formation of ethyl ketipate. Reformatsky, in his work on the synthesis of dibasic hydroxy-acids (A., 1896, i, 206)

found that ethyl α-bromopropionate reacts with ethyl formate with production of ethyl β-hydroxy-αα-dimethylglutarate, but he obtained no evidence of the formation of ethyl formylpropionate corresponding with Fittig and Daimler's ethyl ketipate. In attempting, however, to prepare ethyl β-hydroxyglutarate from ethyl formate and ethyl chloroacetate (A., 1899, i, 516), he obtained ethyl trimesate as the chief product of the reaction, this having been formed by a condensation of ethyl formylacetate. The production of ethyl formylacetate and ethyl ketipate are analogous, and represent the first stage of Reformatsky's synthesis.

These results suggested that perhaps other esters besides ethyl formate and ethyl oxalate might undergo similar condensations with esters of halogen-substituted acids, and this has been found to be the case. The reaction has been applied to ethyl ethoxyacetate, ethyl α-ethoxypropionate, ethyl bromoacetate, and ethyl α-bromopropionate, and the following esters have been obtained: *Ethyl γ-ethoxyaceto acetate*, $OEt \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO_2Et$, b. p. 110°/20—21 mm., 116—120°/26—27 mm., 120—125°/30 mm., and 130—136°/43 mm. *Ethyl γ - ethoxy - α - methylacetoacetate*, $OEt \cdot CH_2 \cdot CO \cdot CHMe \cdot CO_2Et$, b. p. 113—116°/18—20 mm., and 116°/24 mm. *Ethyl γ ethoxy-γ-methylacetoacetate*, $OEt \cdot CHMe \cdot CO \cdot CH_2 \cdot CO_2Et$, b. p. 110—115°/19 mm. *Ethyl γ-ethoxy-αγ-dimethylacetoacetate*, $OEt \cdot CHMe \cdot CO \cdot CHMe \cdot CO_2Et$, b. p. 108—115°/16 mm.   E. G.

Real and Supposititious Oxalomalonic Esters and Applicability of Methanetricarboxylic Ester for Synthetic Purposes. ROLAND SCHOLL and WILHELM EGERER (*Annalen*, 1913, 397, 301—366).— The triethyl oxalomalonate (ethyl ketoethanetricarboxylate) and corresponding acid described by Kurrein (A., 1905, i, 413) are a mixture of ethyl oxalate and malonate, and a mixture of hydrated oxalic acid and malonic acid respectively. Also the substance, b. p. 220°/10 mm., obtained by Bouveault in 1898 from ethyl sodiomalonate and ethyl oxalic chloride, and described by him as triethyl oxalomalonate, $CO_2Et \cdot CO \cdot CH(CO_2Et)_2$, cannot be this compound, as the sequel proves.

[With EMIL HEUSER.]—Methyl dichloromethoxyacetate,
$$OMe \cdot CCl_2 \cdot CO_2Me,$$
which is obtained in 80—90% yield by heating methyl oxalate and phosphorus pentachloride (1½ mols.) at 130—135° for thirty hours, is converted into methyl chloropyruvate, $CO_2Me \cdot COCl$, to the extent of 60% by heating it with a small quantity of platinum black in a bath at 200° until the temperature cannot be raised above 140—160°; the methyl oxalic chloride, b. p. 117—118°, is then removed by distillation, and the residue again heated, a quantity of platinum black being again added if necessary.
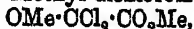
Methyl sodiomalonate and methyl chloropyruvate in equal molecular quantities react in dry ether in a freezing mixture to form methyl malonate and *methyl dioxalomalonate* (*methyl αγ-diketopropane-αββγ-tetracarboxylate*), $C(CO_2Me)(CO \cdot CO_2Me)_2$; after the removal of the ether by a current of air at 25°, the residue is vigorously shaken with ice-water, by which all products are dissolved except the tetracarboxylate.

Methyl dioxalomalonate, m. p. 97·5 —98°, colourless needles or prisms, which can bo also prepared in a similar manner from methyl chloropyruvate and methyl sodio-oxalomalonate (see below), is unattacked by alkaline potassium permanganate or by bromine, and is therefore not an *O*-derivative, $CO_2Me \cdot CO \cdot C(CO_2Me) \colon C(OMe) \cdot O \cdot CO \cdot CO_2Me$ or
$$C(CO_2Me)_2 \colon C(CO_2Me) \cdot O \cdot CO \cdot CO_2Me,$$
but is a very reactive substance in other ways. It is decomposed by water, slowly at the ordinary temperature and rapidly by heating, into oxalic acid and methyl malonate. It is decomposed in the same manner by boiling methyl alcohol, with or without potassium hydroxide. Ammonia, phenylhydrazine, and aniline also decompose the tetracarboxylate, producing methyl malonate and oxamide, oxalic acid diphenylhydrazide, or methyl oxanilate respectively.

By heating at 180—200°, methyl dioxalomalonate loses carbon monoxide and is converted into *methyl oxalomethanetricarboxylate* (*methyl ketoethanetetracarboxylate*), $CO_2Me \cdot CO \cdot C(CO_2Me)_3$, m. p. 91—92°, b. p. 285—286° or 179—180°/15 mm., colourless plates, which is also prepared by heating methyl chloropyruvate and methyl sodiomethanetricarboxylate in benzene (see below). The ester is remarkably stable when heated, being almost unchanged after boiling for one and a-half hours. It does not give a coloration with alcoholic ferric chloride. When boiled with methyl alcohol, the ester is rapidly converted into methyl oxalate and *methyl methanetricarboxylate*, $CH(CO_2Me)_3$, m. p. 45—46°, b. p. 242·7° (corr.) or 128°/15 mm., colourless prisms. Methyl methanetricarboxylate is also obtained by heating a suspension of methyl sodiomalonate in benzene with methyl chloroformate ; it is soluble in dilute sodium hydroxide or carbonate, and forms with methyl-alcoholic sodium methoxide a *sodio*-derivative, $C_7H_9O_6Na$, colourless needles. Methyl methanetricarboxylate exists as the ketonic modification in the crystalline state, but when fused or in alcoholic solution it is partly changed to the enolic form, since the reddish-brown coloration produced by ferric chloride gradually becomes more intense.

Many attempts have been made to prepare methyl oxalomalonate (methyl ketoethane-*aaβ* tricarboxylate) from methyl sodiomalonate and methyl chloropyruvate under different conditions of temperature and concentration, but the principal product is always methyl dioxalomalonate. The desired ester, however, has been obtained from methyl dioxalomalonate by careful decomposition with methyl alcohol or methyl sodiomalonate. The preparation is difficult because methyl oxalomalonate itself is decomposed into methyl oxalate and methyl malonate by methyl alcohol. A 10% solution of methyl dioxalomalonate in benzene is kept with an equal molecular quantity of methyl alcohol for thirty days at the ordinary temperature, or at least four days at 50°, the product is distilled under about 12 mm. pressure, and the ethereal extract of the residue is fractionally crystallised, whereby *methyl oxalomalonate*, $CO_2Me \cdot CO \cdot CH(CO_2Me)_2$, m. p. 49—50°, colourless needles, is obtained, the yield being about 50% of the amount ascertained volumetrically (see below). The ester is also obtained by treating a suspension of methyl sodiomalonate (2 mols.) in benzene at 50° with methyl dioxalomalonate (1 mol.), removing the yellow precipitate (sodio-derivatives of methyl oxalomalonate and methyl

malonate), suspending it in ether at 0°, and treating it with dilute sulphuric acid at 0°; the ester is obtained from the ethereal solution. A third method of preparing methyl oxalomalonate from methyl sodiomalonate and methyl chloropyruvate is described.

Methyl oxalomalonate forms colourless solutions in aqueous sodium hydroxide or carbonate, and does not react in ether with sodium. At 120—130° it decomposes quantitatively into carbon monoxide and methyl methanetricarboxylate, and thus reacts as the ketonic modification. By titration with alcoholic bromine and β-naphthol by Meyer's method, it is shown that the ester is entirely enolic in alcohol or benzene, but contains about 7%, 21%, and 94% (?) of the ketonic modification in chloroform, acetone, and glacial acetic acid respectively. Meyer's method can also be employed to show that the maximum (molecular) percentage of methyl oxalomalonate obtained from equal molecular quantities of methyl alcohol and methyl dioxalomalonate in benzene (at 18° or at 50°) is about 71%.

The series of ethyl esters corresponding with the preceding methyl esters has been prepared. Ethyl sodiomalonate and ethyl chloropyruvate react in ether to form ethyl malonate and a mixture of ethyl oxalo- and dioxalo-malonates, from which the latter cannot be isolated. By distillation under 15 mm. pressure, the mixture decomposes, evolves carbon monoxide, and produces *ethyl methanetricarboxylate*, $CH(CO_2Et)_3$, m. p. 28·5°, and *ethyl oxalomethanetricarboxylate*, $CO_2Et\cdot CO\cdot C(CO_2Et)_3$, b. p. 191—192°/15 mm. (Bouveault's so-called ethyl oxalomalonate).

By treating an ethereal solution of the preceding mixture of ethyl oxalo- and dioxalo-malonates with sodium, *ethyl sodio-oxalomalonate*, $C_{11}H_{15}O_7Na$, is obtained as a white precipitate, from which *ethyl oxalomalonate*, D_4^{17} 1·1147, is obtained. Ethyl oxalomalonate is soluble in dilute sodium hydroxide or carbonate, but is not attacked by sodium except in the presence of a little ethyl malonate. It develops a red coloration with alcoholic ferric chloride, decomposes by heating into carbon monoxide and ethyl methanetricarboxylate, and is decomposed by water or phenylhydrazine in the same manner as the methyl ester.

Ethyl dioxalomalonate, $C(CO_2Et)_2(CO\cdot CO_2Et)_2$, is obtained from ethyl chloropyruvate and ethyl sodio-oxalomalonate in ether, and decomposes by heating.

Conrad and Guthzeit, Michael, and others have tried to utilise methanetricarboxylic esters for synthetic purposes. Their efforts have been unsuccessful, since they used alcohol, by which alkyl methanetricarboxylates are decomposed into alkyl malonates. In the absence of alcohol, alkyl sodiomethanetricarboxylates can be used for synthetic purposes as effectively as ethyl sodioacetoacetate or sodiomalonate, higher temperatures, however, being necessary.

Dimethyl ethyl methanetricarboxylate, $CO_2Et\cdot CH(CO_2Me)_2$, prepared from methyl sodiomalonate and ethyl chloroformate, has b. p. 240—241°, or 138—139°/12 mm., and forms with sodium ethoxide a white *sodio*-derivative. Ethyl sodiomethanetricarboxylate reacts with methyl iodide at 140° to form *ethyl ethane - aaa - tricarboxylate*, $CMe(CO_2Et)_3$, b. p. 250°, or 130°/11 mm., and with ethyl iodide, in a

similar manner, to form *ethyl propane-aaa-tricarboxylate*, $CEt(CO_2Et)_3$, b. p. 258°, or 146°/17 mm.; the latter ester, which has a bitter taste, is converted into ethyl carbonate and ethyl sodioethylmalonate by alcoholic sodium ethoxide.

Ethyl sodiomethanetricarboxylate and acetyl chloride react, finally on the water-bath, to form *ethyl acetylmethanetricarboxylate* (*ethyl β-ketopropane-aaa-tricarboxylate*), $C(CO_2Et)_3 \cdot COMe$, b. p. 253° or 147—148°/14 mm., and with benzoyl chloride to form *ethyl benzoylmethanetricarboxylate*, $C_{17}H_{20}O_7$, b. p. 214°/14 mm. Methyl sodiomethanetricarboxylate and methyl chloro-formate react at 120° to form *methyl methanetetracarboxylate*, $C(CO_2Me)_4$, m. p. 74—75°, b. p. 295° (corr.)/735 mm., or 163°/12 mm., colourless, tasteless needles, which is not attacked by alkaline potassium permanganate or by bromine, and is converted into malonic acid by dilute sulphuric acid and into methyl carbonate and methyl sodiomethanetricarboxylate by alcoholic sodium methoxide. *Dimethyl diethyl methanetetracarboxylate*, b. p. 293°, or 167°/11 mm., and *ethyl methanetetracarboxylate*, m. p. 13·5°, b. p. 304° (corr.)/735 mm., or 173·5°/12 mm., D$_?^?$ 1·0886, both of which have a bitter taste, are also described.

Ethyl oxalomethanetricarboxylate (see above) is also obtained from ethyl sodiomethanetricarboxylate and ethyl chloropyruvate in benzene.

C. S.

Effect of Heating Paraformaldehyde with a Trace of Sulphuric Acid. JOHN G. M. DUNLOP (*Proc. Camb. Phil. Soc.*, 1913, **17**, 180—181).—When a mixture of paraformaldehyde and sulphuric acid is heated at 115° in a sealed tube, bent in such a manner that one end is heated while the other end is kept cool by immersion in a beaker of water, a mobile distillate is obtained, which, when fractionated, yields methyl formate and a liquid, b. p. 95—96°, still under investigation, which appears to be a polymeride of formaldehyde. The yield of methyl formate is very variable and depends on the amount of sulphuric acid and also on the temperature. With about six drops of sulphuric acid to ten grams of trioxymethylene, a yield of about one to two grams of ester appears to be usual. With five grams of acid to the same weight of trioxymethylene, great charring takes place and practically no ester is formed.

H. W.

Methylation of *iso*Valerone by means of Sodamide and Methyl Iodide. Tetramethyl*iso*valerone or βγεεζ-Hexamethylheptan-δ-one. ALBIN HALLER and EDOUARD BAUER (*Compt. rend.*, 1913, **156**, 1295—1298. Compare this vol., i, 488).—By the action of sodamide on *iso*valerone dissolved in benzene, followed by addition of methyl iodide according to the usual method, a liquid was obtained which, after twice repeating this methylation, gave, on fractional distillation, *βγεζ-tetramethylheptan-δ-one*, b. p. 76—78°/13 mm., yielding only traces of an oxime, and *βγγεζ-pentamethylheptan-δ-one*, b. p. 88—89°/13 mm., which gave no oxime, and was not decomposed on boiling with sodamide in benzene. The last substance on further methylation with sodamide and methyl iodide in toluene yielded *βγεεζ-hexamethylheptan-δ-one*, b. p. 107—109°/14 mm., which gave

neither oxime nor semicarbazone, and was not decomposed by sodamide in boiling toluene. On reduction with sodium in alcohol, it yielded the corresponding $\beta\gamma\gamma\epsilon\epsilon\zeta$-*hexamethylheptan-$\delta$-ol*, b. p. 115—117°/13 mm., giving a *phenylurethane*, m. p. 91—92°.   W. G.

Reactions of Methylene. IV. The Decomposition of Ketens at High Temperature. HERMANN STAUDINGER and R. ENDLE (*Ber.*, 1913, **46**, 1437—1442. Compare A., 1912, i, 245)—Since it has been shown (this vol., i, 604) that dicarbon dioxide is incapable of existence, but decomposes into carbon monoxide with rupture of the ethylenic bond, whilst, generally, ethylene derivatives are remarkably stable towards heat, the authors have been led to examine the behaviour of ketens at high temperatures, as these substances form an intermediate link between dicarbon dioxide and the true ethylene derivatives.

The experiments were performed in a quartz tube closed at one end at which the substance was placed. In the middle of the tube a silver spiral was placed which could be maintained at 600—700°. The tube was further connected with a suitable condensing arrangement. Previous to an experiment the tube was exhausted. The substance was then vaporised, and the vapours conducted over the heated spiral.

Diphenylketen, when heated in the above manner, yielded fluorene in accordance with the scheme:

$$(C_6H_5)_2C{:}CO \longrightarrow \frac{C_6H_5}{C_6H_5}{>}C{<} + CO \longrightarrow \frac{C_6H_4}{C_6H_4}{>}CH_2 + CO.$$

Dimethylketen, obtained by heating tetramethyldiketo*cyclo*butane, gave propylene and tetramethylethylene:

$$CMe_2{:}CO \longrightarrow CMe_2{<} \longrightarrow CH_3{\cdot}CH{:}CH_2\,; \quad 2CMe{<} \longrightarrow CMe_2{:}CMe_2.$$

In similar circumstances, diphenylethylene and tetraphenylethylene were not altered, whilst only slight decomposition occurred with diphenyldichloroethylene. Diphenylmethane also underwent no change. At 250°, diphenylbromomethane was converted into tetraphenylethylene and hydrogen bromide. When the silver spiral was replaced by fragments of porcelain, diphenylbromomethane and diphenylchloromethane yielded at 700° tetraphenylethylene instead of fluorene, so that possibly the course of the reaction depends on the contact material.

Phenylcarbimide and phenylthiocarbimide were not affected by a silver spiral at 700°, or by a platinum spiral heated to glowing.
                                                                  H. W.

Esterification of Dihydroxyacetone with Phosphates. ALEXANDER VON LEBEDEV (*Zeitsch. physiol. Chem.*, 1913, **84**, 305).— Polemical (compare Euler and Johansson, A., 1912, i, 750).
                                                                  E. F. A.

The Action of Ultraviolet Light on Sucrose. YNGVE DALSTROM (*Arkiv. Kem. Min. Geol.*, 1913, **4**, No. 30, 1—14).—The source of ultraviolet light was an arc burning between carbon or iron electrodes. The apparatus was similar to that used by Euler and

Ohlén (A., 1911, i, 524), the temperature being 70°. The progress of any reaction taking place was followed by observing the change in rotation of the solutions used, and by titrating any acid formed with standard barium hydroxide solution.

The action of the light of short wave-length produced by the above-mentioned arcs consists, in the first instance, in the formation of an organic acid, which then brings about the hydrolysis of the remaining sucrose. Any direct action of the ultraviolet light on the hydrolysis can only be very small. T. S. P.

Action of Reducing Agents on the Chloraloses. MAURICE HANRIOT and ANDRÉ KLING (*Compt. rend.*, 1913, **156**, 1380—1382).— a- and β-Chloralose and galactochloralose are reduced in aqueous solution by aluminium activated with mercury, one of the chlorine atoms being replaced by hydrogen, and the products obtained are the same as in the action of ammonia on the chloraloses (compare A., 1911, i, 524, 525). In alkaline solution, sodium amalgam removes a second atom of chlorine, and from a-chloralose a *compound*, $C_7H_{11}O_6 \cdot CH_2Cl$, m. p. 168°, is obtained. β-Chloralose yields a similar *compound*, m. p. 166°, giving a *dibenzoyl* derivative, needles, m. p. 149°, and on oxidation with nitric acid it yields a non-crystalline substance giving with hydrazine hydrate a *compound*, $C_7H_7O_5Cl,N_2H_4$, white needles, m. p. 170°.

Sodium in liquid ammonia removes the third chlorine atom from the chloralose, but the product of the action could not be crystallised, the action seeming to lead to the destruction of the chloralose nucleus. W. G.

Pseudo-crystals of Starch and Crystals of Dextrose. GIOVANNI MALFITANO and (Mlle.) A. N. MOSCHKOV (*Compt. rend.*, 1913, **156**, 1412—1415. Compare A., 1910, i, 301, 817).—The so-called crystals of starch, when examined microscopically, although resembling crystals of dextrose fairly closely, are found not to have a true crystalline form. These particles of starch have not the polyhedric form, neither do they exhibit the phenomenon of birefringence. W. G.

The Molecular Size of Dextrin-β. WILHELM BILTZ and WILHELM TRUTHE (*Ber.*, 1913, **46**, 1377—1380. Compare Pringsheim and Langhans, A., 1912, i, 832).—The osmotic pressures exerted by dilute solutions of dextrin-β in a cell composed of collodion impregnated with copper ferrocyanide have been measured directly, and the calculated molecular weights plotted against concentration. By extrapolation for infinite dilution, the value 950 ± 50 is obtained, which confirms the expectation that dextrin-β is a hexa-amylose. The fact that the curve rises rapidly with increasing concentration is not due so much to association as to the time required to reach equilibrium, for higher pressures and therefore lower molecular weights are obtained when the water column is allowed to sink to position than when it is made to rise. The method is being described

in another place. The results obtained for similar substances compare favourably with the values obtained by cryoscopic and other means.   J. C. W.

Cellulose. EDWARD G. PARKER (*J. Physical Chem.*, 1913, **17**, 219—229).—Lange's method of estimating cellulose by hydrolysing the non-celluloses with potassium hydroxide, and the various modifications of it which have been proposed, give untrustworthy results, as the yield of normal cellulose varies with slight variations in the time of boiling, concentration of alkali, and temperature. By heating in a paraffin bath at 130—140° under reflux, after a certain interval of time the yield of normal cellulose from absorbent cotton became constant. The time required for the hydrolysis of the non-celluloses was less with dilute potassium hydroxide within the limits used, a 1 or 2% solution requiring three hours and a 20% solution fifteen hours. It is suggested that the increased evolution of steam from the dilute solutions carried the non-celluloses more rapidly into suspension where the alkali could act on them.

The author's sample of cotton wool contained approximately 92—93% of normal cellulose, 4—5% of soluble cellulose, and 3·25% of water.

Samples of oxycellulose prepared by the action of hydrochloric acid and potassium chlorate and of cellulose reprecipitated from cuprammonium solution contain a much higher proportion of matter soluble in potassium hydroxide. It is suggested that the soluble part of cotton wool consists of oxy- and hydro-cellulose and that cotton reprecipitated from Schweitzer's reagent consists largely of oxycellulose.   R. J. C.

Esters of Cellulose with Benzoic Acid and their Derivatives. G. J. BRIGGS (*Zeitsch. angew. Chem.*, 1913, **26**, 255—256).—Hauser and Muschner have stated (this vol., i, 363) that they were unable to prepare the dibenzoate and tetrabenzoate described by Cross and Bevan. The author gives in detail the methods which were employed in the preparation of these derivatives of cellulose. Both esters are obtained by treating alkali cellulose with a 5—10% solution of benzoyl chloride in benzene, and are separated, first by treating the crude product with chloroform or glacial acetic acid in which the tetrabenzoate dissolves, and then by treating the residue with a cuprammonium solution which removes the unattacked cellulose.   W. H. G.

Oxycellulose. R. OERTEL (*Zeitsch. angew. Chem.*, 1913, **26**, 246—250).—The oxycelluloses prepared by the methods of Witz, Nastukoff, Vignon, or Faber and Tollens are not simple substances. An oxycellulose having properties differing from those already known and described in the literature is obtained by passing an electric current between platinum electrodes and through a solution of potassium chloride containing cellulose in suspension. Under this treatment a large proportion of the cellulose is decomposed and passes into solution, but if the electrolysis is not carried too far, a product

is obtained which is soluble in a 10% solution of sodium hydroxide and has a copper value of 21·0—29·6 according to the extent of the electrolysis, the reducing power becoming greater as the treatment is prolonged. If the electrolysis be carried sufficiently far, the product obtained dissolves in water, forming a stable, colloidal solution, and has a copper value as high as 39·5.

The oxycellulose prepared by the electrolytic method is rapidly destroyed by a hot solution of sodium hydroxide, and when dissolved in a cuprammonium solution gives a very limpid solution. It is converted by sulphuric acid into dextrose, but the yield is not so high as in the case of cellulose, for whereas 100 parts of the latter yield 111 parts of dextrose, 100 parts of oxycellulose yield only 100 parts of dextrose. Oxycellulose when acetylated, using zinc chloride as catalyst, yields an acetate, part of which is soluble in acetone and has $[a]_D - 17°$, and part in chloroform ($[a]_D - 19°$ to $- 20°$); the proportion of acetyl radicle present in the product is not so high as in cellulose triacetate.

The yield of cellobiose acetate from oxycellulose is also not so great as from cellulose. W. H. G.

Formation of Humic Substances by the Action of Polypeptides on Sugars. LOUIS C. MAILLARD (*Compt. rend.*, 1913, **156**, 1159—1160. Compare A., 1912, i, 13, 169; this vol., i, 165).—Glycylglycine like glycine itself readily reacts with xylose and dextrose in the presence of water, with the evolution of carbon dioxide and formation of brown humus-like substances, which are insoluble in boiling water and dilute acids, but partly soluble in ammonia and potassium hydroxide, from which solutions they are reprecipitated on neutralisation. Three samples of commercial peptones behaved similarly with the sugars. W. G.

Some Tetramethylammonium Compounds. JAROSLAV MIL-BAUER (*J. pr. Chem.*, 1913, [ii], **87**, 397—403).—The following tetramethylammonium salts are described: *perchlorate*, white crystals (solubility in cold water 1·126 : 100); *permanganate*, purple-red, tetragonal crystals, which readily decompose on exposure to moist air, and explode violently when heated. The *dithionate*, prepared by the interaction of the sulphate and barium dithionate in aqueous solution, forms lustrous, transparent, colourless cubes and octahedra. The *thiocyanate* crystallises in white, felted needles, the *stannichloride* in white, microscopic octahedra, and the *stannibromide* in pale yellow, microscopic octahedra. The *borate*, $(NMe_4)_3B_4O_7,5H_2O$, forms strongly refractive, transparent crystals, probably belonging to the triclinic system. The *sulphide* and *fluoride* could not be obtained in a pure condition. F. B.

Non-equivalence of the Five Valencies of Nitrogen. JAKOB MEISENHEIMER (*Annalen*, 1913, **397**, 273—300).—The author's explanation of the existence of amine-oxides in enantiomorphous configurations (A., 1912, i, 25) tacitly assumes the non-equivalence of the five valencies of the nitrogen atom. Many facts can be quoted in support

of the assumption, but it has now been definitely proved. Trimethylamine oxide reacts additively with an alkyl iodide, and its hydrochloride reacts with sodium alkyloxide, as follows:

$$Me_3NO + RI \longrightarrow Me_3N{<}^{OR}_{I} \xrightarrow{NaOH} Me_3N{<}^{OR}_{OH} \text{ (I).}$$

$$Me_3NO + HCl \longrightarrow Me_3N{<}^{OH}_{Cl} \xrightarrow{NaOR} Me_3N{<}^{OH}_{OR} \text{ (II).}$$
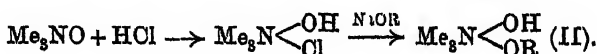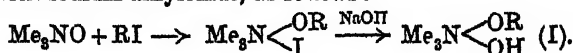
The position of the halogen atom in the ammonium salt is occupied by OH in substance (I) and by OR in substance (II). Several such pairs of isomerides have been prepared, and in every case the two substances are fundamentally different. The substances have not been isolated in the solid state, but by the evaporation of its aqueous solution, substance (I) decomposes quantitatively into trimethylamine, an aldehyde, and water, whereas substance (II) yields trimethylamine oxide and the alcohol R·OH. Pairs of isomerides of the types $Me_3N{<}^{OR}_{OR'}$ and $Me_3N{<}^{OR'}_{OR}$ have also been obtained; the evaporation of their solutions yields trimethylamine, an alcohol, and one aldehyde, the aldehyde always being that corresponding with the alkyl group of the alkyloxy-group not attached to the unique " fifth " valency of the quinquevalent nitrogen atom. Consequently, the two alkyloxy-groups are not attached to the nitrogen atom in the same manner.

The author discusses the constitutions of the isomerides $Me_3N{<}^{OR}_{OR'}$ and $Me_3N{<}^{OR'}_{OR}$, and gives reasons for rejecting formulæ:
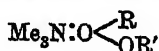
$$Me_3N{:}O{<}^{R}_{OR'}$$

and $Me_3N{:}O{<}^{R'}_{OR}$, $[Me_3NO] \ldots R·OR'$ and $[Me_3NO] \ldots R'·OR$, and $[Me_3N \ldots OR]OR'$ and $[Me_3N \ldots OR']OR$, based on the oxonium, oxonium-ammonium, and (Werner's) ammonium theories respectively. A modification of the last theory is adopted. In Werner's formula of ammonium chloride, the nitrogen atom still remains in a sense tervalent; the four hydrogen atoms are attached to the nitrogen atom each by an amount of affinity less than that corresponding with a principal valency, so that the group NH_4 has an amount of residual affinity whereby it functions as a univalent group and is attached to the acid radicle. Objections can be raised against this view (compare Moore and Winmill, T., 1912, 101, 1673). The author is of opinion that in ammonium compounds the nitrogen is quinquevalent, all five atoms or groups being attached to it by principal valencies, four in an inner, the fifth in an outer, zone; the atom or group in the outer zone is not attached in any definite position, and therefore exerts no influence on the asymmetry of the molecule. The author's pairs of isomerides are consequently represented by the formulæ: $[Me_3N·OR]·OR'$ and $[Me_3N·OR']·OR$, which satisfactorily represent their behaviour.

[With KURT BRATRING.]—Hydrated trimethylamine oxide,

$$NMe_3O,2H_2O,$$

prepared best by Dunstan and Goulding's method (T., 1899, 75, 1005), can be dehydrated by heating under 10—12 mm. at a tempera-

ture not exceeding 150° until the greater part of the water has been
expelled; the temperature is then raised to 190—200°, when *trimethyl-
amine oxide*, NMe_3O, sublimes in colourless needles, m. p. 208°, which
are extremely hygroscopic. By boiling for three-quarters of an hour
with ethyl iodide in ethyl alcohol or with propyl iodide in propyl
alcohol, the anhydrous oxide is readily converted into additive *com-
pounds*, $OEt \cdot NMe_3I$, m. p. 122—125°, and $OPr \cdot NMe_3I$, m. p.
145—147°, respectively, both colourless, crystalline substances. By
treating a dilute aqueous solution of methoxytrimethylammonium
iodide with silver oxide and subsequently with cold hydrochloric acid
and evaporating, *methoxytrimethylammonium chloride*, $OMe \cdot NMe_3Cl$, is
obtained, but the evaporation of an alcoholic solution of the methoxy-
trimethylammonium hydroxide without the addition of hydrochloric
acid results in the formation of trimethylamine (isolated as the
platinichloride) and formaldehyde (isolated as the *p*-nitrophenyl-
hydrazone). Similar results are obtained by the evaporation of
alcoholic solutions of ethoxytrimethylammonium hydroxide and
propoxytrimethylammonium hydroxide, acetaldehyde and prop-
aldehyde, respectively, being formed. By treating trimethylamine
oxide hydrochloride, dissolved in the necessary alcohol, with the
calculated amount of sodium methoxide, ethoxide, or propoxide,
hydroxytrimethylammonium methoxide, ethoxide, and *propoxide* respec-
tively are produced, $OH \cdot NMe_3 \cdot OR$. By evaporation of their alcoholic
solutions, these substances yield no trimethylamine, and only a trace
of an aldehyde; the residue in all three cases is converted into
trimethylamine oxide hydrochloride by alcoholic hydrogen chloride.

[With J. DODONOW.]—*Tetramethylammonium ethoxide,*
$$NMe_4 \cdot OEt, EtOH,$$
hygroscopic crystals, is obtained by treating tetramethylammonium
chloride in anhydrous alcohol with the calculated amount of sodium
ethoxide, adding ether, and removing the sodium chloride by filtration
and the solvent by evaporation in a vacuum at 40°. *Alkyloxytrimethyl-
ammonium alkyloxides*, $[NMe_3 \cdot OR] \cdot OR'$, are obtained in alcoholic
solution by treating alkyloxytrimethylammonium iodides with alcoholic
sodium alkyloxides. The substances have not been isolated, but the
products of their decomposition by the evaporation of their alcoholic
solutions in a current of nitrogen have been examined. *Methoxytri-
methylammonium ethoxide* and *methoxytrimethylammonium propoxide*
each yield formaldehyde, *ethoxytrimethylammonium methoxide* and
ethoxytrimethylammonium propoxide each yield acetaldehyde, whilst
propoxytrimethylammonium methoxide yields propaldehyde.

[By the AUTHOR.]—It is probable that phosphonium compounds
have a constitution similar to that of ammonium compounds suggested
by the author; the existence of phosphorus pentachloride is not
evidence against the probability, since the equivalence of the five
chlorine atoms has not been proved. The additive compound of
phosphenyl chloride and bromine, therefore, should be different from
that of phosphenyl bromide and chlorine, the two substances having
the constitutions $[PPhCl_2Br]Br$ and $[PPhBr_2Cl]Cl$ respectively.
Experiment shows, however, that the two substances are identical.

C. S.

Action of Ethylene Dibromide, Methylene Iodide, and Iodine on Ethyl Aminocrotonate. ERICH BENARY (*Ber.*, 1913, **46**, 1375—1377).—Unlike chloroacetyl chloride, ethylene dibromide and methylene iodide do not form pyrrole derivatives on condensation with ethyl aminocrotonate in presence of pyridine, but they give rise to ethyl dihydrocollidinedicarboxylate and ethyl lutidinedicarboxylate respectively. When iodine is added to the sodium compound of ethylamino-crotonate in ether, *ethyl iodoaminocrotonate*, $NHI \cdot CMe \colon CH \cdot CO_2Et$, is obtained in soft leaflets, m. p. 83—84°, which are hydrolysed by dilute sulphuric acid to ethyl α-iodoacetoacetate (compare ethyl bromo-aminocrotonate, Behrend, A., 1900, i, 210).   J. C. W.

The Reaction Products of Ammonia on Ethyl Dicarbin-tetracarboxylate. ROLAND SCHOLL, KARL HOLDERMANN, and ARMIN LANGER (*Monatsh.*, 1913, **34**, 623—629).—Ethyl dicarbintetracarb-oxylate [ethyl ethylenetetracarboxylate] is best prepared by the method of Blank and Samson (A., 1899, i, 484). It reacts slowly with a saturated alcoholic solution of ammonia at the ordinary temperature, producing *ethyl α-aminoethane-ααββ-tetracarboxylate,*

$$NH_2 \cdot C(CO_2Et)_2 \cdot CH(CO_2Et)_2,$$
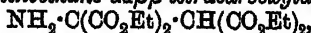
as an additive product. This is an oily liquid, which dissociates into its two components when distilled under reduced pressure and also regenerates ethyl ethylenetetracarboxylate when treated with nitrous acid. The stability of the amino-acid towards acid and alkali is believed to be incompatible with the alternative structure suggested by the two reactions just cited (compare Meister, A., 1888, 675).

If a bomb tube containing a mixture of liquid ammonia and ethyl ethylenetetracarboxylate is kept sealed at the ordinary temperature for sixty hours, tablet or prismatic crystals of *α-aminoethane-ααββ-tetracarboxylamide,* $NH_2 \cdot C(CO \cdot NH_2)_2 \cdot CH(CO \cdot NH_2)_2$, separate. This substance is unstable and smells of ammonia; it is decomposed by water, and when heated alone, gradually decomposes with final carbonisation.   D. F. T.

The Course of the Action of Ammonia on Ethyl Dicarbin-tetracarboxylate. ERNST PHILIPPI and ALFRED UHL (*Monatsh.*, 1913, **34**, 717—731. Compare preceding abstract).—The paper opens with a discussion of various theories as to the mechanism of amide formation.

Carefully dried ammonia was passed for twenty minutes, after all sign of heat evolution had disappeared, into a suspension of ethyl ethylenetetracarboxylate (ethyl dicarbintetracarboxylate) in absolute alcohol, and the resultant solution kept for three months; a yellowish-white, crystalline crust separated. The alcoholic mother liquid con-tained a little unaltered ester together with an oily additive *compound* of molecular proportions of ammonia and ester; *platinichloride,* yellow, microscopic, columnar crystals. The additive compound is believed to be *ethyl α-aminoethane-ααββ-tetracarboxylate,* the presence of the carboxyl groups having so increased the activity of the ethylenic linking of the original ester as to cause addition at this position; such addition of ammonia has been observed at the double bond of several ethylenic esters. When boiled for several hours with 2*N*-hydrochloric

acid, carbon dioxide is set free, leaving the hydrochloride of aspartic acid. A solution of the additive compound in hydrochloric acid when treated with nitrous acid regenerates ethyl ethylenetetracarboxylate; this behaviour is explained by the primary formation of the expected hydroxy-compound, which immediately passes into the ethylenic ester with loss of a molecule of water. The solid crust obtained in the initial experiment consisted of *α-aminoethane-ααββ-tetracarboxylamide*, a hygroscopic, unstable substance which decomposes on moderate heating. Altogether 89·6% of the original ester could be accounted for in the products. D. F. T.

Internally Complex Metallic Salts of Derivatives of Oxalic Acid and of Triformaldoxime. KARL A. HOFMANN and UDO EHRHARDT (*Ber.*, 1913, **46**, 1457—1466).—Various amido-derivatives of oxalic acid have been examined in connexion with the power of formation of internally complex salts, because their structure is such as to suggest an easy formation of a ring composed of five atoms. It is discovered that the stability of the complex salt depends on the number of amido- or imido-groups present, for, of the substances examined, oxamic acid shows least tendency, whilst oxalhydrazide shows the greatest tendency to formation of complex salts. This increase in tendency to form complex salts caused by the increase in supplementary valencies due to the nitrogen atoms accords well with the views of Ley (A., 1905, i, 175) as to the structure of such salts.

As criteria for the occurrence of internally complex salts were accepted an abnormal colour (usually intense), and stability towards alkali and acetic acid. The salts were prepared in each case in alkaline solution, and caused to crystallise by the addition of methyl alcohol.

Oxamic acid under the above conditions gave no complex salt with a nickel, iron, or manganese salt, but with copper acetate and concentrated potassium hydroxide solution, bluish-violet needles of a *potassium-copper* salt, $K_2(NH \cdot CO \cdot CO_2)_2Cu$, were obtained, which are decomposed by excessive alkali or by pure water, yielding copper oxide.

Oxamide gave no compound with iron or manganese, but yielded a *potassium-copper* salt, $K_2(NH \cdot CO \cdot CO \cdot NH)_2Cu,1\frac{1}{2}H_2O$, reddish-violet needles, soluble in alkali to a violet-blue solution, which slowly decomposes, and a *potassium-nickel* salt, $K_2(NH \cdot CO \cdot CO \cdot NH)_2Ni$, bright yellow plates soluble in dilute hydroxide solution to an unstable golden-yellow solution.

Oxalaminohydrazide yielded a *potassium copper* salt, violet-red needles, $K_2(NH \cdot NH \cdot CO \cdot CO \cdot NH)_2Cu,2H_2O$, which, when moist, undergoes gradual decomposition into a basic copper oxamate, and a *potassium-nickel* salt, $K_2(NH \cdot NH \cdot CO \cdot CO \cdot NH)_2Ni$, golden-yellow rods, which dissolve in water to a reddish-yellow solution without decomposition (compare Kerp and Unger, A., 1897, i, 270; Schiff, A., 1902, i, 85).

Oxalhydrazide in strong alkali solution with nickel acetate gives a violet solution, but on crystallisation yellow, hexagonal prisms of a more complex product are obtained; the *potassium-copper* salt,

$$K_2(N_2H_2 \cdot CO \cdot CO \cdot N_2H_2)_2Cu,$$
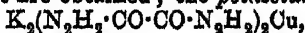
forms bright brown needles, decomp. 270°, soluble in water to a greenish-yellow colour.

Hydroxyloxamide gives a *sodium-copper* salt,

$$Na_4(NH \cdot CO \cdot CO \cdot NO)_2Cu, 4H_2O,$$

reddish-violet needles, and a *sodium-nickel* salt,

$$Na_4(NH \cdot CO \cdot CO \cdot NO)_2Ni, 2H_2O,$$

orange-yellow, hexagonal prisms, which decomposes about 280°. From the composition of these two salts the authors are of the opinion that the salts are derived by displacement of hydroxylic hydrogen, and that under the influence of the alkali used in the process of preparation the $-CO \cdot NH_2$ group undergoes a preceding change into the structure $-C(:NH)OH$. With bivalent and tervalent iron, also, hydroxyloxamide gives yellowish-red alkaline solutions.

Oxalodihydroxamic acid gives a *potassium-copper* salt,

$$K_2(C_4N_4O_8H_3)Cu,$$

brownish-red needles, which decompose at 180°, and a *potassium-nickel* salt, $K_2(C_4N_4O_8H_3)Ni, H_2O$, brownish-yellow needles. Cobalt and iron salts in the presence of excess of alkali give reddish-yellow solutions with oxalodihydroxamic acid.

Formaldoxime is known to give deep colorations with copper, iron, and nickel solutions in the presence of potassium hydroxide (compare Dunstan, T., 1898, **73**, 353), but complex salts have now been isolated for the first time. The colour of the solutions is so intense that manganese, iron, and nickel can be detected at a dilution of one part in a million; the solution of the manganous salt is yellow, but rapidly oxidises in the air to a *manganic* salt, $(CH_2:NO)_3Mn, 2H_2O$., blackish-brown, rectangular plates, which decompose above 220°, and give an intense reddish-brown solution in water. The almost colourless alkaline solution of the nickelous salt in a similar manner absorbs oxygen, yielding a deep brown solution of the *sodium-nickelic* salt,

$$Na_3(CH_2:NO)_6Ni,$$

steel-blue, lustrous crystals, which decompose near 225°. The volume of oxygen absorbed in the two previous oxidations was in good accord with the theoretical. In a similar manner the yellowish red alkaline solution of the ferrous salt undergoes gradual oxidation to the deep violet-red solution of the sodium-ferric salt, which is better obtained by using a ferric salt directly; the *sodium-ferric* salt,

$$Na_2(CH_2:NO)_5Fe, H_2O,$$

forms blue, hexagonal plates, which decompose near 195°. The structure of these salts is believed to be analogous to that of the internally complex salts of the dioximes.   D. F. T.

Synthesis of Parabanic and Substituted Parabanic Acids. HEINRICH BILTZ and ERNST TOPP (*Ber.*, 1913, **46**, 1387—1404).— The authors have effected the synthesis of parabanic and substituted parabanic acids by the action of oxalyl chloride on carbamide and substituted carbamides in ethereal or, more rarely, acetic anhydride solution. Reaction generally takes place smoothly, and the yields, particularly with doubly-substituted carbamides, are excellent. In the case of parabanic acid itself, and, possibly, of dimethylparabanic acid, however, the older methods are simpler and cheaper.

Parabanic acid was obtained in small yield by the action of a boiling ethereal solution of oxalyl chloride on carbamide, and was identified

by conversion into its silver salt. Oxalyldicarbamide, $C_4H_6O_4N_4$, m. p. 270—275° (decomp.), was isolated as by-product. Similar observations have been made by Bornwater (A., 1911, i, 617). Methylparabanic acid, m. p. 153—154°, b. p. 201—202°/13 mm., and oxalyldimethylcarbamide, m. p. 230—232° (decomp.), were similarly prepared from methylcarbamide. An attempt to prepare oxalyl-dimethylcarbamide by melting methylparabanic acid with methyl-carbamide was unsuccessful. Boiling acetic anhydride converted methylparabanic acid into 3-acetyl-1-methylparabanic acid, m. p. 183—185°, which was also obtained by the action of oxalyl chloride on acetylmethylcarbamide. Cold aqueous hydrochloric acid was without action on it, whilst the hot reagent caused great decomposition. Saturation of an absolute alcoholic suspension of it with hydrogen chloride brought about the elimination of the acetyl group, methylparabanic acid being formed in almost quantitative yield.

Dimethylparabanic acid, leaflets, m. p. 154°, b. p. 148—150°/13 mm., was obtained in 70% yield from s-dimethylcarbamide and oxalyl chloride, and also from s-dimethylcarbamide and ethyl chloropyruvate.

Dimethylcarbamide hydrochloride, needles, m. p. 124°, was obtained by saturating a solution of s-dimethylcarbamide in ethyl acetate with hydrogen chloride. *Methylcarbamide hydrochloride*, prepared similarly, is very hygroscopic. It has m. p. about 85—87° after softening at about 70°, and evolves hydrogen chloride at about 125°.

Ethylparabanic acid, m. p. 127—128°, and *oxalyldiethylcarbamide*, needles, m. p. 220—222° (decomp.), were obtained from ethylcarbamide and oxalyl chloride. The properties of the first-named substance differ from those of the ethylparabanic acid described by Andreasch (A., 1898, i, 243).

9-Ethyluric acid glycol (A., 1910, i, 526) was oxidised by potassium dichromate and sulphuric acid to ethylparabanic acid. An attempt was also made to degrade the former substance to the latter in the manner adopted for 7 : 9-dimethyluric acid (Biltz and Krebs, A., 1910, i, 521). An aqueous solution of the glycol was converted by heat into 5-*hydroxy* - 3 - *ethylhydantoylcarbamide*, which was transformed into *3-ethylcaffolide* and ammonium chloride when treated with hydrochloric acid and subsequently evaporated to dryness. When an aqueous solution of 3-ethylcaffolide was boiled, 5-*hydroxy*-3-*ethylhydantoylamide* was formed, which, when oxidised, yielded ethylparabanic acid. The intermediate products could not be obtained in the crystalline state, but the course of the degradation can be deduced from the final product and from the isolation of the by-products expected in the various stages.

Diethylparabanic acid, needles, m. p. 49—51°, b. p. 138—140°/13 mm., was obtained in 78% yield from s diethylcarbamide and oxalyl chloride, and was identical with the product obtained by the degradation of 7 : 9-diethyluric acid glycol (A., 1911, i, 693). Diethylthioparabanic acid had b. p. 148—150°/13 mm.

Phenylparabanic acid, m. p. 213—214° after softening at 208° [Stojentin (A., 1885, 1196) gives m. p. 208°], diphenylparabanic acid, m. p. 202° after previous softening, *benzylparabanic acid*, m. p.,

167—169°, and pp-*bisbromophenylparabanic acid*, $C_{15}H_8O_5N_2Br_2$, were prepared in an analogous manner.

Thiocarbamide reacted vigorously with oxalyl chloride at first, but, even in the presence of a considerable excess of the latter, was not completely converted into *thioparabanic acid*. By repeated crystallisation from ethyl acetate, the latter was obtained in yellowish-red, indistinct crystals, m. p. 215—220° (decomp.), and was further identified by conversion into the *silver* salt, $C_3O_2N_2SAg_2$, and transformation of the latter into 1 : 3-dimethylthioparabanic acid, m. p. 113—115° [Andreasch (A., 1881, 897) gives 112·5°], by means of methyl iodide. When desulphurised by means of hydrochloric or nitric acids, this substance yielded dimethylparabanic acid. Dimethylthioparabanic acid was also prepared by the action of oxalyl chloride on dimethylthiocarbamide, and then had m. p. 113—115°, after softening at 110°, b. p. 153—155°/13 mm.

The authors have also examined the "thioparabanic acid" obtained by Michael (A., 1894, i, 164) by the condensation of thiocarbamide with ethyl oxalate in the presence of sodium ethoxide. They find that it softens at 165°, and has m. p. 173—175° (decomp.). The fusion separates into two layers, the upper one of which begins to distil at about 190°. Since also this substance slowly yields a precipitate with calcium chloride and ammonia, even at the ordinary temperature, the authors are led to the conclusion that it is an additive compound of thiocarbamide and ethyl oxalate (compare Nencki, A., 1874, 981).

Ethylthioparabanic acid was obtained in small yield from ethylthiocarbamide and oxalyl chloride, the loss being chiefly attributable to the difficulty of separating the acid from unchanged ethylthiocarbamide by crystallisation. The observed m. p., 65—69°, is sufficiently close to that found by Andreasch (66°, *loc. cit.*) to prove the identity of the two products. Desulphurisation by means of a boiling alcoholic solution of silver nitrate converted ethylthioparabanic acid into ethylparabanic acid, m. p. 127—128°.

Diphenylthioparabanic acid, pale yellow needles, m. p. 228—230°, was obtained in 94% yield from s-diphenylcarbamide and ethereal oxalyl chloride.   H. W.

Oxalyldicarbamide. HEINRICH BILTZ and ERNST TOPP (*Ber.*, 1913, 46, 1404—1417. Compare preceding abstract, and also Bornwater, A., 1911, i, 617).—When an ethereal solution of oxalyl chloride reacts with finely-powdered carbamide, parabanic acid is formed together with a substance characterised by its very sparing solubility in ordinary solvents, to which the constitution $C_2O_2(NH \cdot CO \cdot NH_2)_2$ is ascribed. This latter substance differs from the oxalyldicarbamide prepared by Grimaux by the fusion of a mixture of parabanic acid and carbamide (A., 1880, 105) in that it gives no biuret reaction, whereas Grimaux's compound yields a faint violet coloration with potassium hydroxide and copper sulphate. Further, oxalyldicarbamide may also be obtained by the oxidation of allantoin in acid solution, 5-hydroxyallantoin being formed as an intermediate product :

$$CO\begin{subarray}{l} \diagup NH \cdot C(OH) \cdot NH \cdot CO \cdot NH_2 \\ \diagdown NH \cdot CO \end{subarray} \longrightarrow C_2O_2(NH \cdot CO \cdot NH_2)_2.$$
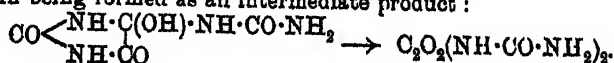
The authors have made a comparative critical examination of these three products, and are led to the conclusion that they are probably identical. The coloration given by Grimaux's compound with potassium hydroxide and copper sulphate is probably due to the presence of some impurity, the nature of which could not be established, but which is neither biuret, oxamide, allantoxanic acid nor allantoxaidine. Certain differences, however, remain unexplained. Thus, oxalyldicarbamide, when acted on by hydriodic acid, yields hydantoin together with other products, whilst, in similar circumstances, Grimaux's compound gives a *substance*, $C_4H_5O_3N_3$, in small quantity. Also, potassium hydroxide transforms all three compounds mainly into oxaluric acid and oxalic acid, but differences are found among the by-products of the action.

Ponomarev's observation (A., 1885, 760) that concentrated potassium hydroxide converts Grimaux's compound into potassium allantoxanate is probably incorrect.

Oxalyldicarbamide was obtained by the oxidation of an aqueous solution of allantoin and sodium acetate by means of ammonium persulphate or by potassium permanganate in dilute acetic acid solution. A portion of the allantoin remained unattacked even when an excess of the oxidising agent was used, whilst, also, oxaluric acid was formed. The latter was isolated in the form of its *ammonium* salt, needles, decomposing at 243—245°, from which the free acid and also the silver salt were obtained.

Grimaux's compound was obtained by heating a mixture of parabanic acid and carbamide and purified by extraction with boiling water. Such preparations yielded with potassium hydroxide and copper sulphate violet colorations of varying intensity. By repeated solution of the product in concentrated sulphuric acid, re-precipitation by means of water, and subsequent repeated extraction with boiling water, substances were obtained which gave only a very faint violet coloration, but the impurity could not thus be completely removed.

All three preparations evolved ammonia at the ordinary temperature when treated with potassium hydroxide (D 1·1—1·4). Under similar conditions oxalyldimethylcarbamide evolved only methylamine, whilst oxalyldiethylcarbamide gave ethylamine. These substances must therefore have the formulæ $C_2O_2(NH \cdot CO \cdot NHMe)_2$ and $C_2O_2(NH \cdot CO \cdot NHEt)_2$ respectively.

When treated with potassium hydroxide under varying conditions, neither of the compounds yielded potassium allantoxanate. Specimens of oxalyldicarbamide, prepared from oxalyl chloride or from allantoin, yielded carbon dioxide, potassium oxalate, and potassium oxalurate. Grimaux's compound yielded mainly potassium oxalurate; sometimes, also, a potassium salt which crystallised in short prisms, became somewhat discoloured at 280°, but was not greatly decomposed at 360°. This salt was probably derived from the impurity which yields the violet coloration, since it gave a distinct violet colour with potassium hydroxide and copper sulphate. In one experiment a second potassium salt, prisms, was obtained, which, with hydrochloric acid, yielded the free acid. The latter was sparingly soluble in water, darkened from 275° onwards, but showed no decomposition point below 360°.

The three compounds were very stable towards acid, and no differences were observed in their behaviour in this respect. Oxalic acid, but no parabanic acid, was obtained from each by the action of boiling fuming nitric acid. Concentrated hydriodic acid (D 1·5) converted Grimaux's compound into oxalic acid. The formation of methyl- and ethyl-parabanic acids by the action of boiling glacial acetic acid on dimethyl- and diethyl-oxalyldicarbamide (compare previous abstract) must be attributed to the formation of the glyoxalone ring during the course of the action, since oxaluric acid itself is partly transformed into parabanic acid by prolonged treatment with boiling glacial acetic acid.

Hydantoin, m. p. 215—217°, and ammonium iodide were obtained by the action of fuming hydriodic acid (D 1·96) at 130—140° on oxalyldicarbamide obtained from oxalyl chloride or from allantoin. Under similar treatment, Grimaux's compound yielded a substance, $C_4H_5O_3N_3$, leaflets, m. p. 270—273° (decomp.), which behaved as a monobasic acid. The *ammonium* salt formed needles, which decomposed at 270—273°. The *silver* salt, $C_4H_4O_3N_3Ag$, was analysed, and appeared to contain a certain amount of silver united to nitrogen.

H. W.

Oxalyl Chloride. V. Oxalyl Bromide and Attempts to Prepare Dicarbon Dioxide. HERMANN STAUDINGER and E. ANTHES (*Ber.*, 1913, **46**, 1426—1437. Compare A., 1912, i, 567).—The authors have prepared oxalyl bromide, which they find to be more readily decomposed by heat and more reactive than the corresponding chloride. In the hope of isolating dicarbon dioxide, CO:CO, they have investigated the action of metals on it. Ready interaction occurs with both zinc and mercury, but in each case carbon monoxide is evolved, so that dicarbon dioxide is probably incapable of existence at the ordinary temperature. With potassium, or the liquid alloy of sodium and potassium, an explosive product is formed, to which the authors attribute the composition OK·C:C·OK.

Phosphorus pentabromide (2 mols.) reacts slowly with anhydrous oxalic acid (1 mol.). If the mixture is warmed, oxalyl bromide is not obtained, nor is the process improved by mixing the materials with sand. If, however, phosphoryl bromide is mixed with phosphorus pentabromide, the dried oxalic acid added, and the mixture maintained at 50° during one day and subsequently distilled, small quantities of oxalyl bromide are obtained. A better method consists in the treatment of well-cooled oxalyl chloride with hydrogen bromide (compare this vol., i, 616), when oxalyl bromide is obtained in 85% yield. It is a greenish-yellow liquid, b. p. 102—103°/720 mm., 16—17°/10 mm., m. p. −19·5°.

A boiling 20% ethereal solution of oxalyl chloride does not react with zinc even after addition of iodine, mercuric chloride, or a trace of water. In ethyl acetate solution, reaction occurs if the zinc has been activated by means of diphenylchloroacetyl chloride. Carbon monoxide is then formed. Mercury, sodium, silver, or magnesium turnings do not react with oxalyl chloride, but a brown precipitate is obtained with magnesium powder in the presence of ether, investigation of

which is incomplete. The vapour of oxalyl chloride is practically completely decomposed by silver at 200°, carbon monoxide being formed. With zinc practically no action occurs.

Oxalyl bromide, on the other hand, is readily decomposed by zinc or mercury at the ordinary temperature, carbon monoxide being formed. Mercurous bromide has no action on it at the ordinary temperature or at 100°. Sodium potassium amalgam reacts with oxalyl bromide without marked development of heat or alteration in appearance. The product, however, explodes violently when subjected to vibration. Attempts to cause potassium to react with oxalyl bromide vapour at 130° or in xylene solution were unsuccessful.

Oxalyl bromide gradually becomes pale reddish-brown when preserved, owing to separation of bromine, decomposition being catalysed by light. At 100° it is stable, but at 150—200° is decomposed into carbon monoxide, bromine, and carbonyl bromide. Oxalyl chloride, on the other hand, could be heated during eighteen hours at 200° without noticeable decomposition occurring; at 340° it is completely decomposed during seventy hours into carbon monoxide and carbonyl chloride.

Oxalyl bromide reacts readily with benzaldehyde in light petroleum solution, forming a white additive *product*, m. p. 131°, with decomposition into benzaldehyde, benzylidene bromide, and carbon monoxide. Under similar conditions an additive *product* is slowly formed from oxalyl chloride, which, when rapidly heated, has m. p. about 212°, but loses carbon monoxide at a lower temperature.

Oxalyl bromide reacts more readily than the corresponding chloride with dimethylaniline, dimethylaminobenzoic acid, crystal-violet and tetramethyldiaminobenzil being formed.

Oxalyl iodide could not be isolated by the action of hydrogen iodide on oxalyl chloride. Even at − 80° only carbon monoxide and iodine were obtained. The latter substances were also produced quantitatively when a solution of oxalyl chloride in ethyl acetate was boiled with sodium iodide.

Unsuccessful attempts were also made to obtain diphenyloxaliminobromide and iodide by the action of the requisite halogen acid on diphenyloxalimino-chloride, $NPh:CCl\cdot CCl:NPh$. The bromide could not be obtained from oxanilide by the action of phosphorus tri- or pentabromide.　　　　　　　　　　　　　　　　　H. W.

An Ester of Hydrocobalticyanic Acid. CHARLES E. BOLSER and L. B. RICHARDSON (*J. Amer. Chem. Soc.*, 1913, **35**, 377—381).— By the action of ethyl iodide on silver cobalticyanide, suspended in alcohol, *ethyl dihydrogen cobalticyanide*, $EtH_2Co(CN)_6, H_2O$, has been obtained as a yellowish-white solid which loses its water of crystallisation at a little over 100° and becomes blue. On the addition of silver nitrate to a solution of the ester, *disilver ethyl cobalticyanide* is produced as a white precipitate; a *copper* salt was also obtained. When the ester is treated with sodium hydroxide, ethylcarbimide is evolved, indicating that the 'ethyl group in some, if not all, of the molecules is attached to nitrogen.

An attempt was made to prepare the corresponding ester of hydroferricyanic acid, but without success.   E. G.

Reaction of Nitroprussides with Acetone. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 376—381).—In this reaction the production of the coloration is accompanied by the production of oximinoacetone, for it is possible to isolate in impure form a coloured salt which yields this compound on treatment with alkali. Analogous results were obtained in the case of acetophenone, a coloured salt being obtained which yielded oximinoacetophenone when treated with alkali.   R. V. S.

Maximum Yield of Amines by the Reduction of Alkyl Cyanides. JITENDRA NATH RAKSHIT (*J. Amer. Chem. Soc.*, 1913, 35, 444—446).—A study of the conditions under which amines are produced by the reduction of nitriles has shown that the best yields can be obtained by the following modification of Ladenburg's method.

The nitrile (5 c.c.) is dissolved in 75 c.c. of alcohol and the solution is introduced in successive quantities of 5 c.c. into a flask containing 5 grams of sodium and attached to a reflux condenser. The mixture is heated at 50—60°. After 20 c.c. of the solution have entered the flask, 5 c.c. of alcohol are added, and the amine evolved on distillation is absorbed in dilute hydrochloric acid. When the whole of the nitrile solution has been introduced, alcohol is added until a layer remains above the solid sodium ethoxide in the flask. When the evolution of hydrogen ceases, the condenser is removed and the flask is connected directly to the absorption apparatus and heated as long as alkaline vapour is produced. If necessary, a further quantity of alcohol is added and the distillation continued. The acid solution is evaporated to dryness on the water-bath, and the amine hydrochloride extracted from the residue with a mixture of alcohol (15 c.c.) and ether (10 c.c.).

The results of experiments with acetonitrile, propionitrile, and butyronitrile show that the amines can be obtained by this method in nearly quantitative yield.   E. G.

Amylene-*iso*nitroamineoxime and **-bisnitroso*iso*nitroamine.** GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 225—231. Compare A., 1911, i, 186).—Cryoscopic molecular weight determinations on the β-nitrosohydroxylamino-β-methylbutan-γ-oneoxime previously described, and on its sodium salt indicate that the compound is probably a bisnitroso*iso*nitroamine. Its formation is probably preceded, however, by that of an *iso*nitroamineoxime which suffers rearrangement and polymerisation. In fact, the freshly prepared substance has m. p. 71°; later, or after recrystallisation, the m. p. is 82°, as formerly stated. Hence it is possible to proceed from oximes of the type $:CX \cdot C:N \cdot OH$ to nitrosyl compounds, $:CX \cdot CH \cdot NO$.

When the bisnitroso*iso*nitroamine is treated with sodium nitrite in aqueous solution, the bisnitroso-oxime, $(NO \cdot CMe_2 \cdot CMe:NOH)_2$, is

formed; the crystals at first melt at 83°, but later on, or after recrystallisation, the m. p. is 140°; the substance is soluble in alkali hydroxides and in acids, and gives a blue coloration with diphenylamine and sulphuric acid.

The *iso*nitroamineoxime previously described yields an *ethyl* ester, $C_7H_{15}O_2N_8$, m. p. 119°, which is prepared by means of the *silver* salt.

The *isonitroamine* of β-methylbutan γ-one, $CMe_2(N_2O_2H)\cdot COMe$, is obtained by the action of hydrochloric acid on the sodium salt of the *iso*nitroamineoxime, or by the action of nitrous acid on β-hydroxylamino-β-methylbutan-γ-one (previously described); it forms large, tabular crystals, m. p. 62°, and gives a blue coloration with diphenylamine and sulphuric acid. The substance has acid properties and is fairly stable, but when heated above its m. p. decomposes, leaving a partially crystalline residue, from which a substance crystallising in quadrangular tablets, m. p. 99°, can be isolated.   R. V. S.

Preparation of Fatty Acids and their Salts containing Arsenic and Phosphorus. FELIX HEINDMANN (D.R.-P. 257641).— When the unsaturated acids of the acetylene series are heated with the halogen derivatives of arsenic or phosphorus, they furnish acidic compounds having a high molecular weight and containing a halogen substituent in addition to phosphorus (or arsenic); they give rise to soluble alkali, and insoluble calcium and strontium salts.

The *compound* produced when stearolic acid and arsenic trichloride (1·5 parts) are heated together at 140° during six hours is obtained (by extraction with ether) as a viscous oil which gradually in part solidifies; it contains As = 11% and chlorine 6—7%; the *strontium* salt, a flesh-coloured powder, contains 12% As; the *calcium* salt is also mentioned.

The *compound* from behenolic acid and arsenic trichloride is a pale brown, viscous oil containing 8—9% As and 5—6% Cl; the *strontium* salt is a colourless powder.

When stearolic acid is heated with an equal quantity of phosphorus trichloride at 140° during fifteen hours, it furnishes two acidic *compounds*; one a viscous, brownish-yellow acid extractable with ether containing P = 4—5% and Cl = 8%; the other an orange-yellow resin insoluble in ether and containing P = 15%. The analogous *compound* from behenolic acid and phosphorus trichloride, and the *strontium* and *calcium* salts are also described, whilst the arsenic and phosphorus chlorides employed can be replaced by the corresponding bromides.   F. M. G. M.

The Benzene Problem. HANS VON LIEBIG (*J. pr. Chem.*, 1913, [ii], **87**, 393—397. Compare A., 1912, i, 686).—A reply to Gebhard's criticism (this vol., i, 28).   F. B.

3 : 3-Dimethyl-[0,1,3]-*dicyclo*hexane. Its Synthesis and Behaviour on Catalytic Reduction. NICOLAI D. ZELINSKI and A. E. USPENSKI (*Ber.*, 1913, **46**, 1466—1474).—The starting point for this substance was 1 : 1-dimethyl*cyclo*hexane-3 : 5-dione, which was prepared by a slight modification of the process of Vorländer (A.,

1897, i, 275); this substance is reduced by the gradual addition of sodium to a hot solution in absolute alcohol with the formation of 1 : 1-*dimethyl*cyclohexane-3 : 5-*diol*, a sweet substance which separates from a mixtuie of benzene and acetone in lustrous, colourless needles. By heating with phosphorus tribromide in a sealed tube at 110—120°, this glycol is converted into 3 : 5-*dibromo*-1 : 1-*dimethyl*cyclohexane, a colourless liquid, b. p. 120—122°/12 mm., D_4^{18} 1·5865, n^{18} 1·5329, which can also be obtained, but less advantageously, by the action of hydrobromic acid on the glycol. Zinc dust acts readily on a warm aqueous-alcoholic solution of this dibromide with the formation of a second ring, the product being 3 : 3-*dimethyl*-[0,1,3]-bicyclo*hexane*,

$$CH_2 {\Large<}{\genfrac{}{}{0pt}{}{CH-CH_2}{CH-CH_2}}{\Large>}CMe_2.$$
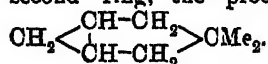
This substance is a colourless liquid, b. p. 115° (corr.), D_4^{20} 0·7962, n^{20} 1·4331, which reacts vigorously with dry bromine, but only slightly with sulphuric acid diluted with half its bulk of water or also with cold dilute potassium permanganate solution. The formation of hydrogen bromide in the first reaction and the lack of change with the other reagents indicate the saturated nature of the hydrocarbon ; in fact, treatment with potassium permanganate solution was resorted to as a means of removing small quantities of an olefinic cyclic hydrocarbon impurity. For the purpose of comparison, the isomeric 1 : 1-dimethyl-Δ^3-*cyclo*hexene (Crossley and Renouf, T., 1905, 87, 1491) was examined, and the following values obtained : b. p. 117—117·5° (corr.), D_4^{20} 0·7994, n^{20} 1·4430, the differences in the density and refractivity indicating the more saturated nature of the new substance.

When 3 : 3-dimethyl-[0,1,3]-*di*cyclohexane is heated with hydriodic acid at 100—110°, an iodo-compound is obtained, which can be reduced in alcoholic solution by zinc dust, yielding a hydrocarbon which from its properties, b. p. 115—116°/760 mm., D_4^{20} 0·7703, n^{20} 1·4223, and its indifference towards permanganate and bromine is probably 1 : 1 : 3-*trimethyl*cyclopentane. That the fission of the trimethylene ring has occurred thus and not at the 2 : 6 linking is evidenced by the distinct nature of the otherwise expected *gem*-dimethylhexamethylene (Crossley, *loc. cit.*). Reduction by hydrogen under the catalytic influence of platinum-black at 125°, or by palladium-black at 55—60°, followed a quite different course, the product, b. p. 109·5—110·5° (corr.), D_4^{20} 0·7403, n^{20} 1·4088, being probably 1-*methyl*-2-*iso*butyl*cyclo*propane. As might be expected (Zelinski, A., 1913, i, 254), reduction by hydrogen under the influence of nickel causes a more considerable change, and even with reduction at 95—100° the physical properties of the product indicate the admixture of the above *cyclo*propane derivative with an appreciable quantity of an octane.   D. F. T.

Anhydrides of Aromatic Sulphonic Acids. HANS MEYER and KARL SCHLEGL (*Monatsh.*, 1913, 34, 561—577).—The action of thionyl chloride on aromatic sulphonic acids presents another example of the very considerable effect of minute traces of foreign substances

on the course and products of a chemical change. The product may be, in this case, the sulphonic anhydride, the sulphonyl chloride, or a mixture of both; the variation is apparently due to traces of impurity in the thionyl chloride, but in the majority of cases investigated no trustworthy decision could be made as to the disturbing factor. The formation of chloride and anhydride appears to be concurrent.

The sulphonic acid anhydrides are colourless or pale yellow, crystalline solids, which are remarkably stable towards water and weak alkali. They react with alcohol, ammonia, and amines, producing the corresponding esters and amides; they can be sulphonated and nitrated. On account of their sparing solubility in indifferent organic solvents they can easily be separated from the very soluble acid chlorides. It is surprising that, although they are stable towards water in bulk, yet they become easily hydrated by moist solvents or by exposure to damp air. The thionyl chloride used for their preparation was purified by distillation over quinoline or dimethylaniline (compare Besthorn, A., 1909, i, 673), the remaining yellow coloration being removed by further successive distillations over linseed oil and pure bees-wax.

Benzenesulphonic acid when heated with excess of thionyl chloride passes into solution with loss of its water of crystallisation, and after further heating, the solution, when cooled, deposits a mixture of benzenesulphonyl chloride with the anhydride, m. p. 90—91° (Billeter, A., 1905, i, 584); the latter substance was usually the preponderating constituent, but occasionally, with apparently the same conditions, the case was the reverse. Silver benzenesulphonate reacts with thionyl chloride yielding the acid chloride as the sole product.

p-*Bromobenzenesulphonic anhydride*, obtained by heating the acid with thionyl chloride and pouring the reaction mixture into ice water, is a colourless, crystalline substance, m. p. 164—167° (decomp.).

2 : 5-*Dibromobenzenesulphonic anhydride*, obtained by a similar process to the last, is a crystalline powder (compare Rosenberg, A., 1886, 551).

m-*Nitrobenzenesulphonic anhydride*, obtained analogously, forms colourless crystals decomposing at 130—140°; the accompanying *chloride* had m. p. 58°.

p-*Toluenesulphonic anhydride*, crystals, m. p. 122—125°, is obtained together with the chloride by heating p-toluenesulphonic acid with pure thionyl chloride; if the thionyl chloride is not pure, the acid chloride is the sole product.

Mesitylensulphonic anhydride is often obtained mixed with the corresponding chloride if mesitylenesulphonic acid is heated with commercial specimens of thionyl chloride. If the last substance has been purified the only product is the acid chloride, but the power to produce the anhydride is restored to the thionyl chloride by distilling it with sulphur chloride. Sodium mesitylenesulphonate behaves in the same curious manner with the various specimens of thionyl chloride.

ψ-*Cumenesulphonic anhydride* is obtained mixed with the corre-

sponding acid chloride under the reverse conditions to those observed in the last case. Purified thionyl chloride gives rise to a mixture of the acid anhydride and acid chloride, whilst the commercial substance yields the acid chloride only.

α-Naphthalenesulphonic anhydride could not be obtained as the corresponding acid and also the sodium salt of the acid were converted by thionyl chloride entirely into the acid chloride.

β-Naphthalenesulphonic anhydride, a pale yellow, crystalline substance, is obtained together with the *chloride*, m. p. 73—74°, by the interaction of β-naphthalenesulphonic acid and excess of thionyl chloride.

α-Anthraquinonesulphonic acid, yellow crystals, m. p. 210—211°, and also the β-isomeride are converted by thionyl chloride entirely into α- and β-anthraquinonesulphonyl chlorides, crystalline solids, m. p. 203—204° and 185—187° respectively.

2-Chloro-5-nitrobenzenesulphonic anhydride forms colourless crystals, m. p. 120—125° (decomp.).

Ethanesulphonic acid with thionyl chloride yielded the acid chloride, whilst 3-pyridinesulphonic acid failed to react.   D. F. T.

Tridiphenylylmethyl. WILHELM SCHLENK (*Ber.*, 1913, **46**, 1475—1481. Compare A., 1910, i, 236).—In reply to Schmidlin (this vol., i, 32) it is stated that the tridiphenylylmethyl obtained earlier by the author (*loc. cit.*) is a homogeneous product, and that the supposed isomeride of Schmidlin is due to an impurity caused by the presence of 4:4'-dibromodiphenyl in the *p*-bromodiphenyl used. In the subsequent Grignard reaction by which the carbinol is produced, the former substance gives rise to 4:4'-*diphenylene-bis-[bidiphenylylcarbinol]*, $OH \cdot C(C_6H_4Ph)_2 \cdot C_6H_4 \cdot C_6H_4 \cdot C(C_6H_4Ph)_2 \cdot OH$, which, mixed with tridiphenylylcarbinol, constitutes Schmidlin's "β-tridiphenylylcarbinol."

4:4'-Diphenylene-bis-[-bidiphenylylcarbinol] can be obtained pure by the condensation of 4:4'-di-iododiphenyl with bisdiphenylylketone and also of ethyl diphenyl-4:4'-dicarboxylate with iododiphenyl, in each case by the Grignard process. The substance is being more closely investigated.   D. F. T.

α-Naphthylbisdiphenylylmethyl. WILHELM SCHLENK and C. BORNHARDT (*Ber.*, 1913, **46**, 1482—1483).—Contrary to the opinion of Schmidlin and Bergmann (this vol., i, 46), *α-naphthylbisdiphenylylcarbinol*, $C_{10}H_7 \cdot C(C_6H_4Ph)_2 \cdot OH$, can be readily obtained by the action of magnesium α-naphthyl bromide on bisdiphenylyl ketone; it forms prismatic crystals, m. p. 228°, which give a bluish-violet solution in sulphuric acid. When heated with a mixture of acetyl chloride and benzene, it is converted into *chloro-α-naphthylbisdiphenylylmethane*, $C_{10}H_7 \cdot C(C_6H_4Ph)_2Cl$, m. p. 214—216°, which gives a deep blue solution in molten phenol. If the chloro-compound is heated in benzene solution with copper bronze under an atmosphere of carbon dioxide, *α-naphthylbisdiphenylylmethyl* is obtained, which separates from its brownish-red benzene solution as a greyish-green, crystalline powder. As a

solution of this substance which has been converted into the peroxide by shaking with air does not regain any of its original colour on keeping, it is probable that the substance is almost entirely unimolecular. D. F. T.

Preparation of Aromatic Nitroamino-compounds. HEINRICH BART (D.R.-P. 258059).—When 3-nitro-4-hydroxyazobenzene-4'-sulphonic acid, $OH \cdot C_6H_3(NO_2) \cdot N \vdots N \cdot C_6H_4 \cdot SO_3H$, is reduced with iodine and sulphurous acid (or phosphorus) it furnishes sulphanilic acid and 3-*nitro*-p-*aminophenol*, glistening. red needles, m. p. 127°, whilst 3-nitro-*p*-aminophenol, together with 4-chloroaniline-3-sulphonic acid, is obtained in a similar manner from 3-nitro-4-hydroxy-4'-chloroazo-benzene-3'-sulphonic acid, $OH \cdot C_6H_3(NO_2) \cdot N \vdots N \cdot C_6H_3 \cdot Cl \cdot SO_3H$.

F. M. G. M.

Preparation of 5-Chloro-6 amino-1-naphthol-3-sulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 258299).—When β-naphthylamine-5 : 7-disulphonic acid is treated with *p*-toluenesulphonyl chloride and the product subsequently chlorinated, it gives rise to 1-*chloro-2-p-toluenesulphonylaminonaphthalene*-5 : 7-*disulphonic acid*, a pale yellow, crystalline powder ; when this is fused at 150—180° with potassium hydroxide, it furnishes 5-*chloro*-6-*p*-*toluenesulphonylamino*-1-*naphthol*-3-*sulphonic acid*, a red, crystalline powder, which when stirred into fuming sulphuric acid yields 5-*chloro*-6-*amino*-1-*naphthol*-3-*sulphonic acid*. F. M. G. M.

Preparation of Creosol (*p*-Hydroxytolyl 3-Methyl Ether). SACCHARIN-FABRIK AKTIENGESELLSCHAFT VORM. FAHLBERG, LIST & Co. (D.R.-P. 258105. Compare A., 1877, ii, 888 ; 1899, i, 346).—When homocatechol is treated with methyl sulphate, it furnishes a 70% yield of pure creosol together with 5—6% of homoveratrole.

F. M. G. M.

Desmotropy of Phenols in the Anthracene Series. ROLAND SCHOLL (*Ber.*, 1913, **46**, 1442).—A claim for priority against Meyer and Schlösser (this vol., i, 295). H. W.

Certain *p*-Toluoylmethyl-, Phenyl-, Nitrophenyl-, Tolyl- and Naphthyl-ethers ; 3-*p*-Tolyl-1 : 4-benzoxazine and 3-*p*-Tolyl-phenmorpholine and their Derivatives. FRANZ KUNCKELL [with KARL PULS] (*Ber. Deut. pharm. Ges.*, 1913, **23**, 269—278).—A series of ethers has been prepared by the action of *p*-tolyl chloromethyl ketone, $C_6H_4Me \cdot CO \cdot CH_2Cl$, on the sodium or potassium salts of phenols.

Phenyl-p-*toluoylmethyl ether*, $C_6H_4Me \cdot CO \cdot CH_2 \cdot OPh$, white needles, m. p. 73—75°, is prepared by boiling an alcoholic solution of *p*-tolyl chloromethyl ketone with an aqueous solution of potassium phenoxide. When dissolved in alcohol and treated with an excess of bromine water, it yields a monobromo-*derivative*, $C_{15}H_{13}O_2Br$, needles, m. p. 105—107°. The similarly prepared p-*nitrophenyl* p-*toluoylmethyl ether* forms pale yellow leaflets, m. p. 165—166°, and is transformed by

phenylhydrazine in acetic acid solution into a somewhat unstable *phenylhydrazone*, yellow needles, m. p. 167—168°.   o-*Nitrophenyl* p-*toluoylmethyl ether* is best obtained by heating an intimate mixture of dry potassium o-nitrophenoxide with p-tolyl chloromethyl ketone at 70°, and crystallises in yellowish-white needles, m. p. 123—124°. p-*Chlorophenyl* p-*toluoylmethyl ether* forms a white, crystalline powder, m. p. 123—124°.   Phenyl p-toluoylmethyl sulphide, m. p. 64°, is obtained by heating a mixture of sodium phenyl sulphide and p-tolyl chloromethyl ketone with light petroleum at 80° during several hours. m-*Tolyl* p-*toluoylmethyl ether*, white leaflets, m. p. 72°, and p-*tolyl* p-*toluoylmethyl ether*, needles, m. p. 101—102°, are similarly prepared.   o-*Tolyl* p-*toluoylmethyl ether*, needles, has m. p. 82°. p-*Toluoylmethyl* β-*naphthyl ether*, prepared by boiling an alcoholic solution of p-tolyl chloromethyl ketone with a solution of β-naphthol in aqueous potassium hydroxide, forms colourless, rhombic crystals, m. p. 82—83°.   The similarly obtained p-*toluoylmethyl* a-*naphthyl ether*, m. p. 99—101°, yields with bromine in acetic acid solution a *compound*, $C_{19}H_{15}O_2Br$, silky needles, m. p. 148—150°.
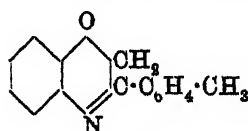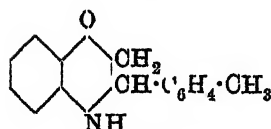
3-p-*Tolyl* 1 : 4-*benzoxazine* (formula I.), m. p. 90—92°, is obtained by the reduction of a cold alcoholic solution of o-nitrophenyl p-toluoylmethyl ether by stannous chloride and fuming hydrochloric acid.   Its *hydrochloride* was analysed.   When the same ether is reduced at a higher temperature by tin and hydrochloric acid, 3-p-*tolylphenmorpholine* (formula II.) is formed in white needles, m. p. 67—68°.   It yields a *nitroso-*derivative, m. p. 101—102°.   The *hydrochloride*, needles, m. p. 190—191°, and the *platinichloride*, m. p. 180—182°, were analysed.

II. W.

Syntheses in the Fatty Aromatic Series. IX.   JULIUS VON BRAUN, A. GRABOWSKI, and G. KIRSCHBAUM (*Ber.*, 1913, 46, 1266—1282.   Compare A., 1912, i, 265 ; 1911, i, 830).—A systematic investigation of the effect of alterations in structure on the odour of the primary alcohols and aldehydes of the phenylethane and phenylpropane groups.   It is found that the introduction of a methyl radicle into the benzene ring has very little effect, but that such substitution at the carbon atom adjacent to the carbinol or aldehyde group of phenylpropyl alcohol or phenylpropaldehyde causes a characteristic change in the odour; substitution of a methyl radicle into the corresponding position of the phenylethane derivatives or at the carbon atom adjacent to the benzene ring in the phenylpropane derivatives produces only a slight weakening of the odour of the parent substances.

m-Xylyl bromide, $C_6H_4Me \cdot CH_2Br$, was converted through the cyanide into tolylethylamine, the benzoyl derivative of which when fused with phosphorus pentachloride and then distilled under reduced

pressure, undergoes decomposition into benzonitrile and m-*tolylethyl chloride*, a colourless liquid of pleasant odour, b. p. 112°/23 mm.; this on heating with sodium acetate and acetic acid for fifteen hours yields the corresponding *acetate*, a liquid of fruity odour, b. p. 130°/18 mm., which is easily hydrolysed to β-m-*tolylethyl alcohol*,

$$C_6H_4Me \cdot CH_2 \cdot CH_2 \cdot OH,$$
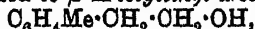
a liquid, b. p. 123—125°/18 mm., D_1^{20} 1·001, of a pleasant odour, resembling that of phenylethyl alcohol.

γ m-Tolylpropyl alcohol can be produced by a process similar to the last, but a more direct method is possible by starting with 6-methylquinoline or 8-methylquinoline; these can be reduced to the corresponding tetrahydroquinoline derivatives, which by the Schotten-Baumann reaction are converted into *benzoyl-6-methyltetrahydroquinoline*, m. p. 78°, and *benzoyl-8 methyltetrahydroquinoline*, needles, m. p. 100°, respectively. If these benzoyl compounds are caused to undergo scission by heating with phosphorus pentachloride (A., 1904, i, 918) they produce *benzo-o-γ-chloropropyl-p-toluidide*, m. p. 151°, and *benzo-o-γ-chloropropyl-o-toluidide*, m. p. 112°, which on cautious hydrolysis by hydrochloric acid in a sealed tube yield the hydrochlorides of o-γ-*chloropropyl-p-toluidine* (*hydrochloride*, m. p. 183°) and o-γ-*chloropropyl-o-toluidine* (*hydrochloride*, m. p. 172°; red *platinichloride*, m. p. 191°). Diazotisation of chloropropyl-p-toluidine hydrochloride, followed by treatment with copper powder, gives rise to 6-*chloro-3-methylphenylpropyl chloride*, $CH_2Cl \cdot [CH_2]_2 \cdot C_6H_3MeCl$, b. p. 125°/9 mm., possessing an odour resembling that of orange rind. If chloropropyl-p-toluidine is diazotised in solution in·sulphuric acid and the reaction product warmed, the resultant *chloropropyl-p-cresol* when heated with alkali loses hydrogen chloride with the formation of 6-*methylchroman*,

$$C_6H_3Me \underset{O——CH_2}{\overset{CH_2 \cdot CH_2}{<}}, \text{ a pale yellow liquid, b. p. } 107°/12 \text{ mm., of}$$
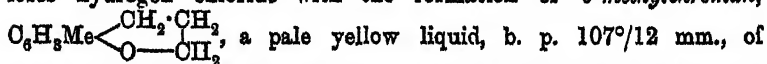
peppermint odour, which gives a red coloration with concentrated sulphuric acid. Reduction of a diazotised solution of the chloropropyltoluidine hydrochloride by an alkaline solution of stannous chloride produces m-*tolylpropyl chloride*, b. p. 130°/14 mm., which can be converted through the *acetate*, b. p. 136°/10 mm., into γ-m-*tolylpropyl alcohol*, $C_6H_4Me \cdot [CH_2]_2 \cdot CH_2 \cdot OH$, b. p. 140°/14 mm., D_1^{20} 0·9609, which closely resembles phenylpropyl alcohol in odour.

The most satisfactory starting point for γ-phenyl-n-butyl alcohol is acetophenone, which by condensation with zinc and ethyl bromoacetate followed by dehydration is converted into β-phenylcrotonic acid; this can be reduced to β-phenyl-n-butyric acid, the *ethyl* ester, b. p. 118°/9 mm., of which can be reduced by sodium and alcohol, giving a 60% yield of γ-*phenyl-n-butyl alcohol*, $CHMePh \cdot CH_2 \cdot CH_2 \cdot OH$, b. p. 134°/16 mm., D_4^{20} 0·9834, which resembles phenylpropyl and phenylethyl alcohols in odour. When heated with hydrochloric acid, the alcohol yields the corresponding *chloride*, b. p. 114—116°/17 mm., which is remarkably resistant to the usual chemical agents; it gives no reaction with potassium acetate and acetic acid, and when treated in light petroleum with aluminium chloride is hardly affected, yielding only traces of a non-volatile hydrocarbon and of a hydrocarbon, b. p.

90—100°/10 mm., possibly methylhydrindene; even with sodium the reaction does not occur normally, as the product is iso*butylbenzene*, b. p. 174—175°, D_4^{20} 0·8625. γ-*Phenyl*-n-*butyl bromide*, b. p. 108—110°/8 mm., can be obtained in a similar manner from the phenylbutyl alcohol, and reacts normally with ethyl sodiomalonate and ethyl sodioacetoacetate as well as with magnesium; the product from its slow reaction with sodium is a mixture of approximately equal quantities of *iso*butylbenzene and βη-*diphenyloctane*, a colourless liquid, b. p. 192—193°/10 mm., D_4^{20} 0·9539, resembling glycerol in appearance. γ-Phenylpropyl bromide, on the other hand, gives with sodium a 75% yield of aζ-diphenylhexane.

γ-*Phenyl*-β-*methylpropyl alcohol*, $CH_2Ph\cdot CHMe\cdot CH_2\cdot OH$, is a rather viscous oil, b. p. 128—129°/16 mm., D_4^{20} 0·9826, with an odour recalling linalool. It is obtained in 65% yield by the reduction of ethyl β-phenyl-a-methylpropionate by sodium and alcohol; the corresponding *phenylmethylpropyl chloride*, b. p. 112—114°/17 mm., is even less reactive than γ-phenyl-n-butyl chloride, for whilst the latter reacts with sodium iodide, the former fails to do so. The *bromide*, b. p. 110°/9 mm., however, behaves in a less abnormal manner, reacting with ethyl sodiomalonate and ethyl sodioacetoacetate; with sodium it reacts slowly, producing *iso*butylbenzene together with βe-*dibenzylhexane*, a viscous oil, b. p. 186—188°/8 mm., D_4^{20} 0·9457.

β-Phenyl-n-propyl alcohol, $CHMePh\cdot CH_2\cdot OH$, can be obtained by the reduction of the corresponding aldehyde (hydratropaldehyde: Claisen, A., 1905, i, 286). An attempt to prepare it through a-phenylethyl bromide by the Grignard reaction miscarried, because the action of magnesium was merely synthetic, producing βγ-diphenylbutane, m. p. 121—122°. The chloride of the above alcohol was prepared by a series of changes, commencing with β-phenyl-n-butyric acid; this reacts with phosphorus pentachloride, producing the acid *chloride*, b. p. 114°/11 mm., which with ammonia in ethereal solution yields the *amide*, m. p. 98·5°; this amide can be converted by the usual process with hypobromite into β-*phenyl*-n-*propylamine*, b. p. 104°/21 mm.; yellow *platinichloride*, m. p. 229° (decomp.); yellow *picrate*, m. p. 180°; *benzoyl* derivative, m. p. 85°. The last-named substance when fused with phosphorus pentachloride, and the mixture distilled under reduced pressure, gives a distillate which on hydrolysis with hydrochloric acid yields β-*phenyl*-n-*propyl chloride*, b. p. 98—100°/22 mm. The same chloride is obtained from benzo-o-β-chloro*iso*-propylanilide (the scission product of 3-methyldihydroindole: von Braun and Kirschbaum, A., 1912, i, 499) by cautious hydrolysis with hydrochloric acid and reduction of the diazo-compound of the resultant o-β-chloro*iso*propylaniline by alkaline stannous chloride solution. The yield of chloride in these two methods of preparation is not very satisfactory, and the product is very unreactive, being completely unaffected by the acetates of the alkali metals or of silver.

β-Phenyl-n-butaldehyde, $CHPhMe\cdot CH_2\cdot CHO$, was prepared by the "nitro" method, because in spite of its lack of reactivity, γ-phenyl-n-butyl chloride will undergo double decomposition with sodium iodide producing γ-*phenyl*-n-*butyl iodide*, a colourless liquid, b. p. 132°/14 mm.; this reacts in the usual manner with silver nitrite, and the reaction

mixture on distillation gives γ-*phenyl*-n-*butyl nitrite*, b. p. approx. 120°/12 mm., and α-*nitro*-γ-*phenyl*-n-*butane*, b. p. 138°/12 mm. The latter substance when treated in alcoholic solution with an equimolecular quantity of sodium hydroxide solution, and then with a solution of stannous chloride in hydrochloric acid, produces an oil which, after boiling with dilute sulphuric acid, yields β-*phenyl*-n-*butaldehyde*, b. p. 110°/9 mm.; *phenylhydrazone*, oily; the odour of the substance is sharp, and recalls that of phenylacetaldehyde.

D. F. T.

Cholesterol. XVI. Methyl *iso*Hexyl Ketone, a Degradation Product of Cholesterol. ADOLF WINDAUS and C. RESAU (*Ber.*, 1913, **46**, 1246—1248).—It has been observed by many workers that the oxidation of cholesterol by various methods is always accompanied by the formation of a substance of pleasant odour (compare Windaus, A., 1909, i, 920). The odoriferous substance has now been isolated by collecting the distillate from a boiling solution of cholesteryl acetate in acetic acid to which a solution of chromic acid was gradually added; acetic acid was removed from the distillate by sodium hydroxide solution, the liquid was again distilled, then dissolved in ether, and the acetone removed by shaking with water. Careful evaporation of the ether then gave a small residue of the pleasant smelling oil; *semicarbazone*, colourless, rectangular leaflets, m. p. 153—154°.

The composition, $C_9H_{19}ON_3$, of the semicarbazone suggested that the parent substance is an octanone, and a comparison of the m. p.'s of the semicarbazones indicated that the odoriferous substance was methyl *iso*hexyl ketone. For further confirmation, methyl *iso*hexyl ketone (Darzens, A., 1905, i, 172) was prepared (p-*nitrophenylhydrazone*, deep yellow crystals, m. p. 83°), and the identity of the semicarbazones was satisfactorily established.

D. F. T.

Preparation of Alkali Salts of *m*-Hydroxyphenoxypropane-sulphonic Acid. ALBERT WOLFF (D.R.-P. 258473).—*Sodium γ-chloro-β-hydroxypropane-α-sulphonate*, $CH_2Cl\cdot CH(OH)\cdot CH_2\cdot SO_3Na$, hard, colourless crystals, is obtained when a boiling aqueous solution of sodium sulphite (252 parts) in 500 parts of water is treated with 128 parts of α-dichlorohydrin.
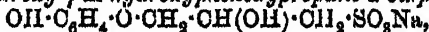
Sodium β-hydroxy-γ-m-hydroxyphenoxypropane-α-sulphonate,
$$OH\cdot C_6H_4\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot SO_3Na,$$
a colourless, crystalline powder, can be prepared in 90% yield by heating a concentrated solution of catechol (110 parts) in 56 parts of sodium hydroxide with 196 parts of the foregoing sodium chlorohydroxypropanesulphonate during two hours under reflux in the presence of an indifferent gas such as hydrogen.

F. M. G. M.

Aromatic Telluretine Compounds. I. KARL LEDERER (*Ber.*, 1913, **46**, 1358—1362).—Diphenyl telluride has been condensed with bromoacetic acid and its esters, and compounds analogous to dimethylthetine bromide (Brown and Letts, A., 1874, 980) and to phenylmethylselenetine bromide (Pope and Neville, T., 1902, **81**, 1553) have been

obtained. The corresponding purely aromatic derivatives of sulphur and selenium could not be prepared.

Diphenyl telluride and methyl bromoacetate were left together for two or three days and then precipitated with ether. The *methyl* ester of *diphenyltelluretine bromide*, $TePh_2Br\cdot OH_2\cdot CO_2Me$, formed stout prisms from hot water, m. p. 105—106°. It was transformed by silver chloride into the *chloride*, m. p. 115—116°, with which zinc, gold, mercuric and platinic chlorides formed *double* salts. The *chromate* and *dichromate* could not be recrystallised, but the *picrate*,

$$C_6H_2(NO_2)_3\cdot O\cdot TePh_2\cdot CH_2\cdot CO_2Me.$$
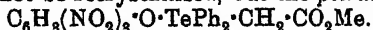
formed well-defined, yellow needles, m. p. 144—145°. The *ethyl* ester, m. p. 63—64°, from ethyl bromoacetate was resolved by boiling water into its components. *Diphenyltelluretine bromide*, $TePh_2Br\cdot CH_2\cdot CO_2H$, itself was obtained from bromoacetic acid as a very hygroscopic mass, which, on shaking with silver oxide, gave *diphenyltelluretine*,

$$OH\cdot TePh_2\cdot CH_2\cdot CO_2H,$$
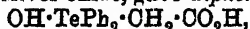
in the form of needles, m. p. 117—118°. The esters were hydrolysed by, and gave the same compound with, silver oxide.   J. C. W.

Preparation and Reactions of Acid Haloids. HERMANN STAUDINGER and E. ANTHES (*Ber.*, 1913, **46**, 1417—1426).—Acid chlorides can be converted into the corresponding bromides or iodides by the action of an excess of hydrogen bromide or hydrogen iodide, the reaction being interpreted according to the scheme :

$$R\cdot COCl + HI \rightleftharpoons R\cdot CClI\cdot OH \rightleftharpoons R\cdot COI + HCl.$$

The analogous reaction with hydrocyanic acid does not appear to be applicable to the production of nitriles.

Acetyl chloride was converted into almost pure acetyl bromide by the action of dry hydrogen bromide, the yield being 80%. Similarly, cooled acetyl chloride and hydrogen iodide gave a 70% yield of acetyl iodide, b. p. 105—108°. *Diphenylacetyl iodide*, pale yellow crystals, m. p. 46°, obtained from hydrogen iodide and diphenylacetyl chloride, was far more sensitive to the action of moisture than the latter substance, and, when heated at 150°, was decomposed with an almost quantitative elimination of carbon monoxide.

Benzoyl chloride was incompletely transformed into the bromide at the ordinary temperature; completely, however, at 100°. Benzoyl iodide was readily obtained in 95% yield from benzoyl chloride and hydrogen iodide. It had b. p. 109—109·5°/10 mm., and was colourless when pure, rapidly becoming yellow when preserved. The rate of decomposition of the benzoyl haloids by water has been investigated by shaking dilute ethereal solutions with water at 0° and titration of the acid formed. The iodide was found to be more readily decomposed than the bromide, and the latter more readily than the chloride. It was also noticed that elimination of the halogen acid was incomplete (compare Straus and Hüssy, A., 1909, i, 490). This was attributed to decomposition of the benzoyl haloid by ether, but no ethyl iodide and only traces of ethyl benzoate could be detected. When ether was replaced by toluene or xylene, sharp differences in the behaviour of the haloids could not be detected, probably owing to the slight solubility of water in the hydrocarbons. When heated in a sealed tube for twenty

hours at 190°, benzoyl iodide yielded iodine, benzoic acid, and black, asphalt-like products, but no carbon monoxide. At 250°, carbon monoxide was not liberated. At 500°, however, under 15—25 mm. pressure, benzoyl iodide yielded iodobenzene and iodine, whilst at 700° still more pronounced decomposition occurred. Benzoyl bromide was stable at 500°, but yielded bromobenzene at 700°, whilst decomposition of benzoyl chloride did not occur even at 700°.

Benzoyl iodide reacted vigorously with benzaldehyde with formation of *iodobenzyl benzoate*, $Ph \cdot CO_2 \cdot CHIPh$. The product so obtained was contaminated with iodine and could not be purified owing to its extreme instability. It was obtained, however, in colourless crystals, m. p. about 60°, by mixing the reagents in light petroleum solution. Benzoyl bromide reacted slowly with benzaldehyde, bromobenzyl benzoate, m. p. 65°, being formed, whilst no compound was obtained from benzoyl chloride.

Benzoyl iodide was scarcely affected by treatment with dry hydrogen chloride for three hours, but, after fifteen hours, the presence of benzoyl chloride was ascertained.

Benzoyl iodide reacted slowly with mercury at the ordinary temperature. At 120—130° reaction was complete within two to three days. Benzil did not appear to be formed. The main products, particularly at the higher temperature, were brown resins and a *substance*, m. p. 40°, which has not yet been investigated. In benzene solution, reaction occurred more slowly. In ethereal solution a ready action was observed, the products of which were ethyl iodide and ethyl benzoate.

Hydrogen bromide did not react with carbonyl chloride even at 200°. Slight reaction was observed when hydrogen iodide was mixed with gaseous carbonyl chloride.

Hydrogen cyanide appeared to be without action on boiling acetyl chloride or on oxalyl chloride at 15—20°. H. W.

The **Perkin Reaction.** HANS MEYER and ROBERT BEER (*Monatsh.*, 1913, **34**, 649—658).—In spite of the earlier investigations, it is still not certain whether in the Perkin synthesis the reaction occurs between the aldehyde and the salt of the fatty acid, or whether the anhydride plays a primary part.

It is now demonstrated that the yield of unsaturated acid depends largely on the aldehyde used; with sodium acetate and acetic anhydride, o-iodobenzaldehyde, o-chlorobenzaldehyde, o-nitrobenzaldehyde, benzaldehyde and p-dimethylaminobenzaldehyde gave yields in decreasing order of magnitude; with potassium acetate and acetic anhydride the relative behaviour of the various aldehydes appears to be the same, but the yields are uniformly better.

A comparison of the yields obtained by using o-chlorobenzaldehyde with the acetates of various metals in the presence of acetic anhydride shows that the alkali metals give better results the higher the atomic weight; lead acetate gives results comparable with the acetates of the alkali metals; mercuric acetate is poorer, whilst the acetates of copper and of the alkaline earth metals produce very small yields of chlorocinnamic acid.

The presence of an acid anhydride is not indispensable; benzaldehyde heated for twenty-six hours with potassium acetate and acetic acid gives a 30% yield of cinnamic acid. The yields of unsaturated acid when o-chlorobenzaldehyde is heated with an acetate and acetic acid is usually somewhat smaller than when acetic anhydride is used, but rubidium and lead acetates gave actually slightly better yields with the acid than with the anhydride. Michael's view (A., 1901, i, 358) that the Perkin reaction occurs between aldehyde and acid anhydride is, therefore, untenable.

The rôle of the acetic acid in the immediately preceding experiments appears to be merely that of solvent, and it is found that a 40% yield of unsaturated acid can be obtained by heating together o-chloro-benzaldehyde and potassium acetate, without the addition of a third substance, to 240° for thirty-six hours.   D. F. T.

The Halogen-Substituted Cinnamic Acids and their Behaviour in Ultra-violet Light. RICHARD STOERMER and PAUL HEYMANN (*Ber.*, 1913, **46**, 1249—1266. Compare A., 1912, i, 974).— In reply to Liebermann (this vol., i, 265), the authors submit that the former's proof of the structure of *allo*-cinnamic acid is not above suspicion, and that the nature of his experiments renders his decision merely a probability. The action of sulphuric acid on *allo*-cinnamic acid yields only ordinary cinnamic acid, and even if fuming sulphuric acid is used, the main product under suitable conditions is ordinary cinnamic acid accompanied by a relatively very small quantity of truxone (compare Liebermann, A., 1898, i, 662). It is also already recognised that there are exceptions to Liebermann's method of deciding the constitution of these isomerides by physical properties.

The main portion of the paper consists of the results of an extension of the investigation of the behaviour of ethylenic stereoisomerides in ultra-violet light (Stoermer, A., 1911, i, 295; 1910, i, 114).

α-Chlorocinnamic acid (Sudborough and James, T., 1906, **89**, 107), m. p. 137° (*aniline* salt, needles, m. p. 137°), exposed in acetic acid solution to the ultra-violet rays from a mercury lamp for twenty-one days is converted to the extent of 21% into *allo*-α-chlorocinnamic acid, m. p. 111° (*aniline* salt, needles, m. p. 96°). In a similar manner in methyl alcoholic solution, α-chlorocinnamamide, m. p. 121°, is converted to the extent of 10% into the amide (m. p. 134°) of the *allo*-acid in ten days.

α-Bromocinnamic acid, m. p. 131° (*aniline* salt, needles, m. p. 132°), when exposed in acetic acid to ultra-violet rays for twenty-one days is converted to the extent of 10% into *allo*-α-bromocinnamic acid, m. p. 120° (*aniline* salt, scales, m. p. 102°). When a methyl alcoholic solution of the *allo*-acid was exposed to ultra-violet rays, 71% was converted into the more stable isomeride. Similarly, α-bromocinnamamide, leaflets, m. p. 117°, in methyl-alcoholic solution is converted into the *allo*-isomeride (needles, m. p. 129°; 24% in 240 hours); the latter substance under similar treatment is re-converted to the extent of 50% into the original amide.

β-Bromocinnamic acid, needles or leaflets, m. p. 135°, is readily pro-

duced by submitting the *allo*-isomeride (Erlenmeyer, A., 1896, i, 46) in chloroform solution containing a little bromine to the action of sunlight; the product is an equilibrium mixture. The action of ultra-violet rays on an acetic acid solution for thirty-five days converted 40% of the acid into the *allo*-isomeride, m. p. 159—160°. Ultra-violet illumination converted 75% of the *allo*-acid in ethyl acetate solution into the ordinary acid.

Of the two β-chlorocinnamic acids, m. p. 142° and 132° respectively, the latter from its similarity to the analogous bromo-compound must be the *allo*-isomeride (compare Michael and Pendleton, A., 1889, 1063). The acetic acid solution of the former (*trans*-) compound is converted to the extent of 40% in twenty-one days into the *allo*-isomeride; the *aniline* salt, like that of *allo*-β-bromocinnamic acid, is unstable. In contact with bromine in sunlight the *allo*-acid is slowly re-converted into the other form.

The authors discontinue the use of the term *allo* in connexion with the αβ-dihalogen-substituted cinnamic acids, because the compounds which from their power of indone formation must be the *cis*-isomerides are more stable than the *trans*-isomerides.

cis αβ-Dichlorocinnamic acid, m. p. 121° (*aniline* salt, needles, m. p. 129°), when treated with cold sulphuric acid yields dichloroindone.

When a solution in acetic acid is submitted to ultra-violet rays for twenty-one days, 45% of the acid undergoes conversion into the hitherto unknown trans-*αβ-dichlorocinnamic acid*, rhombic tablets, m. p. 101°; *barium* salt, woolly needles; *aniline* salt, needles, m. p. 121°. The *trans*-acid is also obtained by the elimination of hydrogen chloride from the dichloride of α-chlorocinnamic acid by the action of potassium hydroxide solution; it is separated from the *cis*-isomeride simultaneously formed by the sparing solubility of the *potassium* salt of the *trans*-acid in alcohol. The action of sunlight on a chloroform solution of the *trans*-acid containing a little bromine causes a re-conversion into the *cis*-isomeride.

The action of bromine on phenylpropiolic acid solution in carbon disulphide in the absence of sunlight produces a mixture of *cis*-αβ-dibromocinnamic acid, yellow prisms, m. p. 100°, with the isomeric *trans*-acid, scales, m. p. 136°, in approximately the proportion 2 : 1; the two acids give *aniline* salts, needles, m. p. 126° and 128° respectively. In chloroform solution containing bromine, sunlight causes a partial change of the *trans*- into the *cis*-isomeride, but as the latter always predominates in the equilibrium mixture, it may be regarded as the more stable (compare Roser and Haselhoff, A., 1888, 1304). In ultra-violet light, the *cis*-acid, dissolved in acetic acid, is converted into the *trans*-acid to the extent of 40% in fourteen days. This *cis*-acid is converted by cold sulphuric acid into dibromoindone, but a much better method for the production of this substance is the action of aluminium chloride on the corresponding acid chloride in carbon disulphide solution at water-bath temperature; under these conditions a quantitative yield of dibromoindone, m. p. 123°, is obtained.

αβ-Di-iodocinnamic acid, m. p. 171° (Liebermann and Sachse, A., 1892, 470), decomposes when exposed in solution to ultra-violet rays; consequently no isomerisation could be detected; from the fact that the

known acid gives no indone formation with sulphuric acid, it is presumably of the *trans*-configuration.

Curves are given illustrating the course of the isomerisation of the acids, and the properties of the various acids are tabulated.

D. F. T.

The Constitution of Abietic Acid. PAUL LEVY (*Zeitsch. anorg. Chem.*, 1913, **81**, 145—155).—The evidence for the constitution of abietic acid is reviewed and a few new experiments described. Oxidation with nitric acid yields dinitropropane and *trans-cyclo*hexane-1 : 2-dicarboxylic acid. Abietic acid is related to retene and pinene, contains a *cyclo*hexane ring and an *iso*propyl group, and has its carboxyl group attached to a tertiary carbon atom. None of the formulæ hitherto proposed conforms to all these conditions, with the exception of that due to Easterfield and Bagley (T., 1904, **85**, 1241).

C. H. D.

Benzoylated Cyanohydrins and Amides from Aldehydes, and the Corresponding Hydroxy-acids JULES ALOY and CHARLES RABAUT (*Bull. Soc. chim.*, 1913, [iv], **13**, 457—460. Compare A., 1912, i, 462).—The preparation of benzoylated cyanohydrins by the action of benzoyl chloride on a mixture of an aldehyde with aqueous potassium cyanide has been extended to the fatty and heterocyclic series.

Benzoylglycollonitrile [*Benzoyloxyacetonitrile*], $OBz \cdot CH_2 \cdot CN$, from formaldehyde, forms well-defined, stable crystals, m. p. 26—27°, b. p. 275° or 165°/25 mm., which dissolve in concentrated hydrochloric acid or slightly warmed 60% sulphuric acid with the formation of *benzoyloxyacetamide*, $CO \cdot NH_2 \cdot CH_2 \cdot OBz$, in hard, lustrous crystals, m. p. 117—118°. Hydrolysis by hot dilute sodium hydroxide provides a convenient method for the preparation of glycollic acid, but when an insufficient quantity of very dilute alkali is employed and the reaction is arrested as soon as ammonia ceases to be liberated, benzoyloxyacetic acid, m. p. 79°, results. The *silver* salt was analysed. Alcoholic ammonia converts the nitrile into benzamide and the amide into benzamide and glycollamide. Sodium ethoxide causes no replacement by sodium in the $-CH_2$ group, but yields sodium cyanide and benzoate and ethyl benzoate, and in the case of benzoylmandelonitrile gives rise to benzoin.

Similarly, a-benzoyloxybutyronitrile is obtained from propaldehyde as an impure oil, which gives a *benzoyloxybutyramide*, $OBz \cdot CHEt \cdot CO \cdot NH_2$, m. p. 92°, and finally sodium a-hydroxybutyrate on hydrolysis, whilst *a-benzoyloxyisovaleronitrile*, $CHMe_2 \cdot CH(OBz) \cdot CN$, from *iso*butaldehyde, has m. p. 21—22°, and gives the *amide*, m. p. 98°, and then a-hydroxy-*iso*valeric acid on hydrolysis. *Benzoyloxyfurylacetonitrile*,

$$C_4H_3O \cdot CH(OBz) \cdot CN,$$
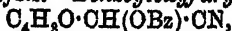
from furfuraldehyde, has m.p. 47—48°, but hydrolysis led to discoloured, indefinite substances.

The reaction is being extended to the ketones, in which case prolonged agitation is necessary (compare Francis and Davis, T., 1909, **95**, 1403 ; 1910, **97**, 949). J. C. W.

Racemisation of Tropic Acid and its Esters, together with a Theory of Racemisation, Substitution, and the Walden Inversion. JOHANNES GADAMER (*J. pr. Chem.*, 1913, [ii], 87, 312—392).—This paper contains a full and detailed account of the author's theory, a short description of which has already appeared (A., 1912, i, 934; compare Frankland, Presidential Address, T., 1913, 103, 722—725).

[With MAX KUNTZE.]—*Ethyl l-tropate*, prepared from ethyl iodide and silver *l*-tropate, has $[a]_D^{12}$ - 47 5° in alcoholic solution; the d-*ester* has $[a]_D^{14}$ + 46·6°.

Experiments are also described to show that the conversion of hyoscyamine into atropine is due to ionisation at the asymmetric atom.

F. B.

Preparation of an Inner Anhydride (Lactam) of 2-Aminobenzoyl-*o*-benzoic Acid. AKTIEN-GESELLSCHAFT FUR ANILIN-FABRIKATION (D.R.-P. 258343).—When the 2-aminobenzoyl-*o*-benzoic

(I.)

(II.)

acids of the general formula I (where X and Y may be hydrogen, methyl, a halogen or carboxylic group) are heated either alone with condensing agents or with solvents of high boiling point, they readily lose water and furnish inner anhydrides (lactams) of general formula II, and which are readily hydrolysed by alkali hydroxides to regenerate the parent substance.
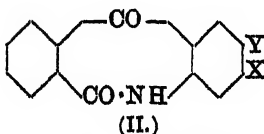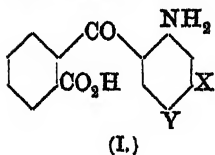
When 2-*aminobenzoyl-o-benzoic acid*, rhombic crystals, m. p. 195° (with formation of the lactam), is heated at 200° with nitrobenzene it furnishes the corresponding lactam, m. p. 245°; the base accompanied by another isomeride is obtained by the nitration and subsequent reduction of benzoyl-*o*-benzoic acid and separation effected by means of the *calcium* salts.

2 : 5-*Diaminobenzoyl* o-benzoic acid, yellow needles, m. p. 265°, is obtained by heating 2-*amino-5-acetylaminobenzoyl-o-benzoic acid* (prepared by the nitration and subsequent reduction of 3-acetylaminobenzoyl-*o*-benzoic acid) with 30% sulphuric acid and subsequent decomposition of the *lactam* thus formed.

2-*Amino-5-acetylamino-4-carboxybenzoyl-o-benzoic acid*, yellow needles, m. p. 315°, is obtained by the oxidation (with potassium permanganate) of 2-*nitro-5-acetylamino-4-toluoyl-o-benzoic acid* and reduction of the so-obtained 2-*nitro-5-acetylamino-4-carboxybenzoyl-o-benzoic acid*, m. p. 247°; when heated with 30% sulphuric acid, the foregoing amino-acetylamino-base furnishes the *sulphate* of 2 : 5-*diamino-4-carboxybenzoyl-o-benzoic acid*, m. p. 340° (about), together with its *lactam*.

F. M. G. M.

Reduction of the Anhydrides and Imides of Phthalic and Naphthalic Acids. ARNOLD REISSERT (*Ber.*, 1913, 46, 1484—1491). —The reduction of phthalic anhydride by zinc dust and acetic acid is known to give a complex mixture, from which diphthalyl, hydro-

diphthalyl-lactonic acid and phthalide can be isolated (Wislicenus, A., 1885, 57), whilst reduction by distillation with zinc dust yields a mixture of zinc phthalate and diphthalyl.

It is now discovered that when phthalic anhydride is gradually introduced into an agitated suspension of zinc dust in a solution of calcium chloride in 40% alcohol at 20—22° about half is converted into phthalic acid and half into diphthalyl-lactonic acid, for which the author prefers the formula $CO\diagdown\diagup_{C_6H_4}^{O}\diagup CH\cdot CO\cdot C_6H_4\cdot CO_2H$.

No satisfactory method for the preparation of phthalide from phthalic anhydride could be discovered, but it was found that phthalimide can be reduced by stirring with a suspension of zinc dust in cold $2N$-sodium hydroxide solution with the production of *hydroxyphthalimidine* (compare Graebe, A., 1885, 979), $C_6H_4\diagup_{CO}^{CH(OH)}\diagdown NH$, needles, m. p. 171—172°, which on boiling with acetic acid is converted into a *substance*, needles, m. p. 240—241°, of which the structure is probably $CO\diagdown_{NH}^{C_6H_4}\diagup CH—C(OH)\diagup_{CO}^{C_6H_4}\diagdown NH$. If after the reduction of phthalimide to hydroxyphthalimidine the reaction mixture containing excess of zinc is heated, a further reduction occurs and ammonia is liberated with the production of phthalide, $C_6H_4\diagup_{CH_2}^{CO}\diagdown O$, in almost theoretical yield.

If naphthalic anhydride is shaken with zinc dust and $2N$-sodium hydroxide solution, a blue solution is obtained, which on addition of more alkali and further shaking becomes red; on neutralisation a reddish-yellow, crystalline *substance*, $C_{24}H_{12}O_5$, m. p. 213—215°, is precipitated, whilst the naphthalic acid produced simultaneously remains in solution. The coloured reduction product, which the author designates *deoxynaphthalic anhydride*, possibly of the formula $CO\diagdown_{C_{10}H_6}^{O}\diagup C—C\diagup_{C_{10}H_6}^{O}\diagdown CO$, gives an unstable blue colour with

sodium carbonate solution and a stable red one with sodium hydroxide; on mixing intimately with concentrated ammonia solution the substance is converted into a *compound*, for which the annexed structure is suggested; this is a yellowish-red substance, which dissolves in alkali solutions with a bright blue or violet colour.

$)(OH)—C\diagdown_{C_{10}H_6}^{O}\diagup CO$
$\quad | \quad$
$\quad NH$

$CO\diagdown_{C_{10}H_6}^{O}\diagup C(OH)\diagup^{C}\diagdown_{C_{10}H_6}^{O}\diagup CO$

The reduction of naphthalimide by a similar process to that which was successful with phthalimide yielded only a pasty product.

D. F. T.

Action of Acylamino-acid Chlorides on the Sodium Compounds of the Esters of Malonic and Cyanoacetic Acids. Siegmund Gabriel (*Ber.*, 1913, 46, 1319—1358).—A number of

phthaliminoacylmalonic esters of the series

$$C_8H_4O_2{:}N{\cdot}CXY{\cdot}CO{\cdot}CH(CO_2R)_2,$$
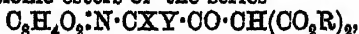
where X and Y = H or alkyl, have been prepared from acylamino-chlorides. It is found that the stability of the esters is enhanced when X and Y represent 1 or 2 alkyl groups, the non-substituted compounds having the character of strong acids and losing one $-CO_2R$ group on boiling with water (A., 1909, i, 491; 1911, i, 212). The presence of these groups is also 'a criterion for the pyrrolone condensation (A., 1911, i, 227), which also occurs when the malonic ester group is replaced by $-CH_2{\cdot}CN$, $-CH_2{\cdot}CO{\cdot}NH_2$, or by methyl, and when a benzoyl nucleus is substituted for the phthalyl group.

The same substituted phthaliminoacylmalonic esters are peculiar in their behaviour towards sodium alkyloxides, for the yellow sodium compound of the ester changes into the colourless neutral salt of a strong acid. Phenoxyacylmalonic esters underwent no such isomerism, whereas benzoylamino*iso*butyryl chloride condensed with methyl sodiomalonate to form a strongly acid compound with one methyl alcohol group less than the expected malonic ester. Benzoylmethyl-amino*iso*butyryl chloride, on the other hand, gave the malonic ester, from which it appears that an unsubstituted imino-group is necessary for the formation of the acidic compounds. These are shown to be derivatives of tetramic acid (Anschütz, A., 1912, i, 836), and their formation from methyl phthalimino*iso*butyrylmalonate, for example, presupposes the preliminary opening of the phthalyl ring and the addition of alcohol according to the scheme :

$$C_6H_4{<}^{CO}_{CO}{>}N{\cdot}CMe_2{\cdot}CO{\cdot}CH(CO_2Me)_2 + R{\cdot}OH$$

$$= CO_2R{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CMe_2{\cdot}CO{\cdot}CH(CO_2Me)_2$$

$$= CO_2R{\cdot}C_6H_4{\cdot}CO{\cdot}N{<}^{CO\text{----}CH{\cdot}CO_2Me}_{CMe_2{\cdot}CO} + CH_3{\cdot}OH.$$
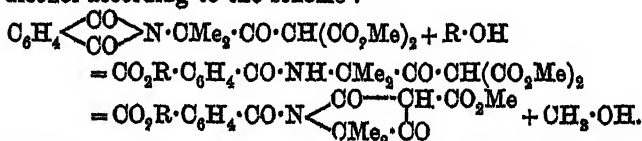
This is supported by synthesis and by the fact that the methyl ethyl ester obtained from the methyl malonate and sodium ethoxide on the one hand, and from the ethyl malonate and sodium methoxide on the other, were isomeric. All these tetramic acid derivatives lose the ester group which is attached to the tetramic acid ring on hydrolysis with very dilute acids, and are decomposed by hydriodic acid into phthalic acid, alkyl iodide, carbon dioxide, and aminomethylbutanone.

[With JAMES COLMAN and KARL A. BÖTTCHER.]—For the preparation of ethyl phthalimino*iso*butyrylmalonate (A., 1911, i, 213), it is recommended to use enough ethyl sodiomalonate to form the *sodium* compound of the new ester. This forms light yellow needles, and gives a yellow, alkaline solution"which is decomposed by carbon dioxide. The ethyl alcoholic solution or the solution of the free ester mixed with sodium ethoxide gradually becomes pale in the cold, quickly on warming, and on evaporation deposits the white, isomeric *sodium* salt, $C_{19}H_{20}O_7NNa$, which gives a neutral solution and is only decomposed by mineral acids, when *ethyl carbethoxybenzoyldimethyltetramcarboxylate* [2 : 4-*diketo-1-benzoyl-5 : 5-dimethylpyrrolidine-o-3-dicarboxylate*],

$$CO_2Et{\cdot}C_6H_4{\cdot}CO{\cdot}N{<}^{CO\text{----}CH{\cdot}CO_2Et}_{CMe_2{\cdot}CO}\text{ , is formed as a crystalline}$$
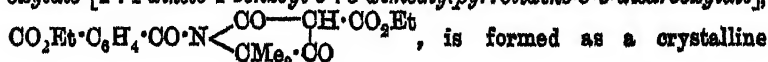
powder, m. p. 81°. It has a strongly acid reaction, gives an orange-red colour with ferric chloride, and yields the *tetramic acid*,

$$CO_2Et \cdot C_6H_4 \cdot CO \cdot N \underset{CMe_2 \cdot CO}{\overset{CO——CH_2}{\big<}},$$
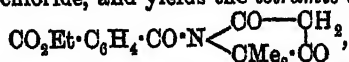
on hydrolysis with warm dilute hydrochloric acid as a white powder, m. p. 198—199°, which disengages carbon dioxide from barium carbonate, gives a red coloration with ferric chloride, and an *ammonium* salt, in slender, white needles. The acid gives with one molecule of bromine the *monobromide*,

$$CO_2Et \cdot C_6H_4 \cdot CO \cdot N \underset{CMe_2 \cdot CO}{\overset{CO——CHBr}{\big<}},$$
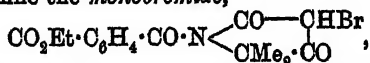
m. p. 159—160°, from glacial acetic acid, which forms a hydrate with $1H_2O$ in rhombic needles, m. p. 121—122°, from dilute acetic acid, and yields phthalic acid and *bromoaminomethylbutanone hydrobromide*, $CH_2Br \cdot CO \cdot CMe_2 \cdot NH_2,HBr$, in leaflets, m. p. 156°, on boiling with hydrobromic acid. This ketone reduces Fehling's solution and forms a *picrate*, which gives a turbid liquid at 135° becoming clear at 147°. Excess of bromine gives the *dibromide*, $C_{16}H_{15}O_5NBr_2$, m. p. 155°, which is neutral and can no longer become enolic. Chlorine yields the neutral *dichloride* in flat needles, m. p. 126—126·5°, from which the *hydrochloride* of *dichloroaminomethylbutanone*,

$$CHCl_2 \cdot CO \cdot CMe_2 \cdot NH_2,HCl,$$
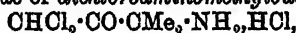
m. p. 203°, was obtained. The *oxime*,

$$CO_2Et \cdot C_6H_4 \cdot CO \cdot N \underset{CMe_2 \cdot C:N \cdot OH}{\overset{CO——CH_2}{\big<}},$$
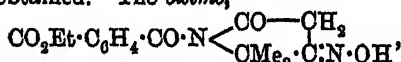
forms microscopic crystals, m. p. 193°.

When the initial ethyl malonate is treated with sodium methoxide or when the sodium compound is left with methyl alcohol, the white, microcrystalline, neutral *sodium* salt, $C_{18}H_{18}O_7NNa$, is obtained, from which hydrochloric acid precipitates *ethyl carbomethoxybenzoyldimethyltetramcarboxylate* [*methyl ethyl* 2 : 4-*diketo*-1-*benzoyl*-5 : 5-*dimethylpyrrolidine*-o-3-*dicarboxylate*], $CO_2Me \cdot C_6H_4 \cdot CO \cdot N \underset{CMe_2 \cdot CO}{\overset{CO——CH \cdot CO_2Et}{\big<}}$, which forms colourless needles, m. p. 133—134°, gives a *copper* and a *silver* salt, and, on hydrolysis, the *tetramic acid*, $C_{15}H_{15}O_5N$, in needles, m. p. 210—211°. The acid distils unchanged in a vacuum, yields an *ammonium* salt, an *oxime*, $C_{15}H_{16}O_5N_2$, in sparkling prisms, m. p. 210°, and a *hydrazone*, $C_{15}H_{17}O_4N_3$, in short prisms, m. p. 222—223°. The *methyl ether*, $CO_2Me \cdot C_6H_4 \cdot CO \cdot N \underset{CMe_2 \cdot C \cdot OMe}{\overset{CO——CH}{\big<}}$, is obtained by the action of methyl alcohol and hydrogen chloride as a crystalline powder, m. p. 103—104°, which gives no colour with ferric chloride, is insoluble in alkalis, and yields a *bromo*-derivative, $C_{16}H_{16}O_5NBr$, in matted needles, m. p. 140°. The *acetyl* compound,

$$CO_2Me \cdot C_6H_4 \cdot CO \cdot N \underset{CMe_2 \cdot C \cdot OAc}{\overset{CO——CH}{\big<}},$$
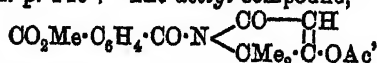
forms crystalline granules, m. p. 119—120°. The *monobromo*-derivative forms flat, rectangular prisms, m. p. 221°, which yield an *ammonium* salt and the above bromoaminomethylbutanone hydro-

bromide. The *dibromo*-derivative forms glistening needles, m. p. 193°, and the *dichloride*, m. p. 172—173°, yields the above dichloroaminomethylbutanone salt on hydrolysis.

Methyl phthaliminoi-obutyrylmalonate,

$$C_8H_4O_2:N\cdot CMe_2\cdot CO\cdot CH(CO_2Me)_2,$$
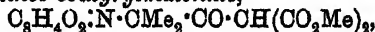
forms colourless, rhombohedral crystals, m. p. 91°, which give a dark cherry-red colour with ferric chloride. The *sodium* compound is yellow, reacts alkaline, and changes in methyl alcohol into the colourless, neutral *isomeride*, from which hydrochloric acid liberates *methyl carbomethoxybenzoyldimethyltetramcarboxylate* [2 : 4-*diketo*-1-*benzoyl*-5 : 5-*dimethylpyrrolidine*-o-3-*dicarboxylate*],

$$CO_2Me\cdot C_6H_4\cdot CO\cdot N{<}^{CO——CH\cdot CO_2Me}_{CMe_2\cdot CH},$$
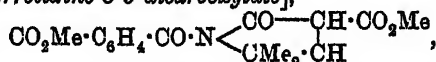
in short, thick columns, m. p. 155°, which may be distilled in a vacuum. It forms a *silver* salt, and gives the above tetramic acid, m. p. 210—211°, on hydrolysis. In order to synthesise the compound, α-amino*iso*butyric acid was condensed with the chloride of methyl hydrogen phthalate (Meyer, A., 1901, i, 750) to form *carbomethoxybenzoylamino*iso*butyric acid*, $CO_2Me\cdot C_6H_4\cdot CO\cdot NH\cdot CMe_2\cdot CO_2H$, in rhombic tablets, m. p. 168°. This was converted into the *chloride* by means of thionyl chloride, and then condensed with methyl sodiomalonate and the product identified with the expected ester, m. p. 155°. When the methyl ester, m. p. 91°, is allowed to react with sodium ethoxide, the neutral *sodium* salt of *methyl carbethoxybenzoyldimethyltetramcarboxylate*,

$$CO_2Et\cdot C_6H_4\cdot CO\cdot N{<}^{CO——CH\cdot CO_2Me}_{CMe_2\cdot CO},$$
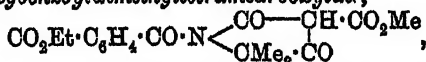
is formed as a granular powder, m. p. 99°, which gives a *copper* salt. In contrast to its isomeride, m. p. 133—134°, its tetramic acid derivative is the ethyl compound, m. p. 199°, and not the methyl, m. p. 210—211°.

The methyl ester, m. p. 91°, but not so the isomeride, m. p. 155°, condenses in presence of methyl sodiomalonate in boiling benzene to *methyl benzoylenedimethylpyrrolonecarboxylate*,

$$^{C_6H_4\cdot C:C(CO_2Me)}_{CO—N\cdot CMe_2}{>}CO,$$
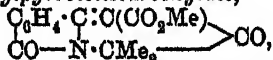
in yellow needles, m. p. 165° (compare the ethyl ester, A., 1911, i, 213). Similarly, phthaliminomethylbutanone (*ibid.*) gave benzoylenedimethylpyrrolone (A., 1911, i, 228). *Methyl phthalimino*iso*butyrate*, $C_8H_4O_2:N\cdot CMe_2\cdot CO_2Me$, prepared from the chloride in colourless, rhombic plates, m. p. 78°, combined with methyl alcohol when left with that liquid or when warmed with sodium methoxide solution, and gave the *methyl* ester of *methyl phthalamino*iso*butyrate*

$$CO_2Me\cdot C_6H_4\cdot CO\cdot NH\cdot CMe_2\cdot CO_2Me,$$
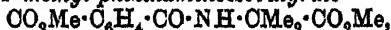
in delicate needles, m. p.˙116—117°, thus behaving differently, as was expected, from the phthaliminoacetates and propionates, which give *iso*quinoline derivatives (A., 1900, i, 358). The methyl ester, m. p. 91°, may also be methylated by the action of methyl iodide on the sodium compound. *Methyl phthalimino*iso*butyrylmethylmalonate*,

$$C_8H_4O_2:N\cdot CMe_2\cdot CO\cdot CMe(CO_2Me)_2,$$
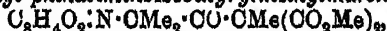
forms prisms, m. p. 121°, and on hydrolysis with hydrochloric acid yields *aminomethylpentanone hydrochloride*, $C_2H_5\cdot CO\cdot CMe_2\cdot NH_2,HCl,$

in rectangular tablets, m. p. 164°.   The *hydriodide*, $C_6H_{13}ON,HI$, crystallises in needles, m. p. 141—142°, and gives a *picrate*, m. p. 145°. The *benzoyl* derivative forms silky needles, m. p. 118°, and the *phthalyl* compound crystallises in rhombic tablets, m. p. 70°, whilst the free *base*, $C_2H_5 \cdot CO \cdot CMe_2 \cdot NH_2$, is a colourless, mobile liquid, which, unlike aminomethylbutanone, but like amino*iso*butyrophenone (A., 1911, i, 212), distils without condensation, b. p. 157·5°/762 mm.

α-Phthalylalanyl chloride (A., 1908, i, 182) has also been con-densed with ethyl sodiomalonate, forming a light yellow *sodium* compound, from which carbon dioxide separated *ethyl α-phthalylalanyl-malonate*, $C_6H_4O_2{:}N \cdot CHMe \cdot CO \cdot CH(CO_2Et)_2$, in rhombic plates, m. p. 73—74°. Contrary to the above phthaliminoisobutyrylmalonates, it did not form a tetramic or a pyrrolone derivative. When hydrolysed by means of fuming hydriodic acid, methyl α-aminoethyl ketone *hydriodide*, C_4H_9NO,HI, m. p. 89°, is formed (Künne, A., 1895, i, 685), but hydrobromic acid at 70° led to *α-phthaliminoethyl methyl ketone*, $C_8H_4O_2{:}N \cdot CHMe \cdot COMe$, which formed flat leaflets, m. p. 85—86°.

Phenoxyacetyl chloride was also condensed with methyl sodio-malonate, when the new *sodium* salt was obtained in silky, white needles, from which carbon dioxide separated *methyl phenoxyacetyl-malonate*, $OPh \cdot CH_2 \cdot CO \cdot CH(CO_2Me)_2$, as an oil.

Similarly, *phenoxyisobutyryl chloride*, $OPh \cdot CMe_2 \cdot COCl$, a colourless oil, b. p. 112—113°/12·5 mm., yielded *ethyl α-phenoxyisobutyrylmalonate*, $OPh \cdot CMe_2 \cdot CO \cdot CH(CO_2Et)_2$, in prisms, m. p. 69°. The chloride was obtained from ethyl phenoxy*iso*butyrate, b. p. 127°/12 mm. (compare Bischoff, A., 1900, i, 346), by the action of phosphorus pentachloride on the free acid, and yielded the *amide*, $OPh \cdot CMe_2 \cdot CO \cdot NH_2$, in silky needles, m. p. 116°.
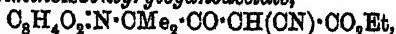
*Ethyl α-phthalimino*isobutyrylcyanoacetate,
$$C_8H_4O_2{:}N \cdot CMe_2 \cdot CO \cdot CH(CN) \cdot CO_2Et,$$
was obtained by adding phthalimino*iso*butyryl chloride to ethyl sodio-cyanoacetate suspended in benzene, and decomposing the new light yellow salt with hydrochloric acid. It forms flat leaflets, m. p. 111°, and has acidic properties, giving an *ammonium* salt,
$$C_{17}H_{15}N_2O_5,NH_4,H_2O,$$
and a *copper* salt. On hydrolysis with dilute hydrochloric acid it yields *α-phthalimino*isobutyryl*acetonitrile*, $C_8H_4O_2{:}N \cdot CMe_2 \cdot CO \cdot CH_2 \cdot CN$, in long needles, m. p. 154°. When left or warmed with dilute alkalis the substance loses water and forms *o-benzoylenecyanodimethylpyrrolone*,
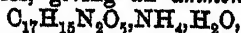
$$\underset{CO—N \cdot CMe_2}{\overset{C_6H_4 \cdot C{:}C(CN)}{\Big>}} CO$$ in yellow prisms, m. p. 273°, which are con-

verted by hydrobromic acid into benzoylenedimethylpyrrolone (*loc. cit.*). The nitrile also dissolves in cold concentrated sulphuric acid with the formation of *phthalimino*isobutyryl*acetamide*,
$$C_8H_4O_2{:}N \cdot CMe_2 \cdot CO \cdot CH_2 \cdot CO \cdot NH_2,$$
in long, flat needles, m. p. 130°. This compound condenses very readily to *o-benzoylenedimethylpyrrolonecarbonamide*,

$$\underset{CO—N \cdot CMe_2}{\overset{C_6H_4 \cdot C{:}C(CO \cdot NH_2)}{\Big>}} CO,$$
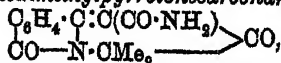
which forms long, yellow prisms, m. p. 217°. When warmed with

concentrated sulphuric acid, however, the nitrile takes up $2H_2O$ and forms the *phthaloylic acid* derivative of *amino*isobutyrylacetamide (o-*carboxybenzoylamino*isobutyrylacetamide),

$$CO_2H \cdot C_6H_4 \cdot CO \cdot NH \cdot CMe_2 \cdot CO \cdot CH_2 \cdot CO \cdot NH_2,$$
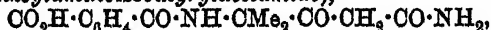
as a crystalline powder, m. p. 171°, which merely dissolves and undergoes no condensation in alkalis.

Benzoylamino*iso*butyric acid (dimethylhippuric acid) was prepared by benzoylating amino*iso*butyric acid in acetone in presence of pyridine and then converted into the chloride (Mohr, A., 1910, i, 117). The latter was condensed with methyl sodiomalonate, when the expected ester was not obtained, but rather *methyl benzoyldimethyltetra*carboxylate [2 : 4-*diketo*-1-*benzoyl*-5 : 5-*dimethylpyrrolidine*-3-*carboxylate*],

$$\begin{array}{c} NBz \cdot CO \cdot CH \cdot CO_2Me \\ CMe_2 \!\!-\!\! CO \end{array}$$

, which forms rhombic tablets or short prisms, m. p. 154—155°. The substance had an acid reaction, dissolved in ammonia, and gave a *copper* salt and an orange-red coloration with ferric chloride. Hydrolysis with hydrochloric or hydriodic acid gave the salts of aminomethylbutanone. The analogous *ethyl* ester, $C_{16}H_{17}O_5N$, forms short prisms, m. p. 111°. Condensation of the above chloride with ethyl cyanoacetate, however, followed a normal course, and led to *ethyl benzoylamino*isobutyrylcyanoacetate, $NHBz \cdot CMe_2 \cdot CO \cdot CH(CN) \cdot CO_2Et$, which formed colourless rhombohedra, m. p. 165°. The compound forms salts with ammonia and silver, and gives a cherry-red coloration with ferric chloride. Hydrolysis with hydrochloric acid leads to *benzoylamino*isobutyrylacetonitrile, $NHBz \cdot CMe_2 \cdot CO \cdot CH_2 \cdot CN$, which forms long needles.

For the condensation of malonic esters with benzoylmethylamino*iso*butyryl chloride, methylamino*iso*butyric acid, prepared by a modification of Zelinsky and Stadnikoff's general method (A., 1906, i, 425), was benzoylated as above, the *benzoylmethylamino*isobutyric acid, $NMeBz \cdot CMe_2 \cdot CO_2H$, short prisms, m. p. 183°, was treated with thionyl chloride, and the crude product left with methyl sodiomalonate. *Methyl benzoylmethylamino*isobutyrylmalonate,

$$NMeBz \cdot CMe_2 \cdot CO \cdot CH(CO_2Me)_2,$$
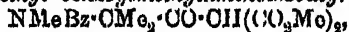
forms colourless, short columns, m. p. 125°. It is gradually resolved into its components by boiling water, but is not only hydrolysed, but, furthermore, condensed by hydriodic acid to *phenyltrimethylpyrrolone*,

$$\begin{array}{c} CPh \!\!: \!\! CH \cdot CO \\ NMe \!\!-\!\! CMe_2 \end{array}$$

. This base crystallises in hexagonal tablets, m. p. 100°, b. p. 346—347°/768 mm., and forms a soluble chloride, a sparingly soluble nitrate, iodide and picrate, m. p. 147°, and a platinichloride.   J. C. W.

Condensation of Pyromellitic Anhydride with Benzene and with Toluene. II. ERNST PHILIPPI (*Monatsh.*, 1913, **34**, 705—717. Compare A., 1911, i, 793 ; Mills and Mills, T., 1912, **101**, 2194).—It has not been found possible to produce substances analogous to anthranol in the dinaphthanthracene group by intramolecular elimination of water from reduced derivatives of dibenzoylbenzenecarboxylic acids.

In the condensation of dibenzoylbenzenedicarboxylic acids to diphthaloylbenzene by concentrated sulphuric acid, 2-*benzoylanthraquinone*-

3-*carboxylic acid*, m. p. 283—285°, is obtained as a by-product, but by allowing the reaction to proceed at a lower temperature for a shorter period this substance becomes the main product; the *sodium* and *potassium* salts are sparingly soluble. Reduction of the acid with ammoniacal zinc dust and copper sulphate solution gives a poor yield of 2-*benzylanthracene*-3-*carboxylic acid*, m. p. 235—237°, which can be further reduced by hydriodic acid and phosphorus to 1 : 5-*dibenzyl-benzene*-2 : 4-*dicarboxylic acid*, which decomposes without melting. No dianthranol nor any other condensation product could be obtained by heating this substance with sulphuric acid.

Reduction of diphthaloylbenzene by distillation with zinc dust in an atmosphere of hydrogen under reduced pressure and also by alkaline hyposulphite yielded a sparingly soluble, reddish-brown, crystalline solid; this was unaltered by a temperature of 360°, and from the presence of two hydroxyl groups the structure is probably

$$C_6H_4\!\!<\!\!^{CO}_{CO}\!\!>\!\!C_6H_2\!\!<\!\!^{C(OH)}_{C(OH)}\!\!>\!\!C_6H_4.$$
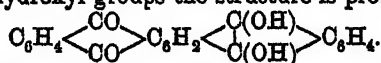
The product of reduction of diphthaloylbenzene with hydriodic acid and phosphorus was exceedingly difficult to purify; it is an almost colourless *substance*, m. p. 210—215° (decomp.), the composition of which indicates a formula $C_{22}H_{20}$.

The condensation of pyromellitic anhydride with toluene by means of aluminium chloride proceeds in exactly the same way as with benzene; the reaction product is a mixture of two acids of the structure $C_6H_5Me\cdot CO\cdot C_6H_2(CO_2H)_2\cdot CO\cdot C_6H_3Me$, namely, 1 : 5 - *di* - p - *toluoyl-benzene* - 2 : 4 - *dicarboxylic acid* and 1 : 4-*di*-p-*toluoyl*-2 : 5-*benzene-dicarboxylic acid*, which can be separated by fractional crystallisation from nitrobenzene; the former acid has m. p. 245—248°, whilst the latter and less soluble acid decomposes without melting. Reduction of the more soluble isomeride by zinc dust and copper in alkaline solution is exceedingly slow, and yields only the *lactone*,

$$O\!\!<\!\!^{CH(C_6H_4Me)}_{CO}\!\!-\!\!>\!\!C_6H_2\!\!<\!\!^{CH(C_6H_4Me)}_{CO}\!\!-\!\!>\!\!O,$$
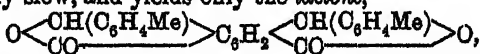
a yellow solid which does not melt below 240°. The same lactone is also obtained when the reducing agent is a mixture of phosphorus and hydriodic acid, but in this case it is accompanied by 1 : 5-*di*-p-*tolylbenzene*-2 : 4-*dicarboxylic acid*, a yellow solid, m. p. near 238°.

<div align="right">D. F. T.</div>

Hydrogenation of Santonin in Presence of Palladium Black. GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 443—447). —The action of hydrogen on an alcoholic solution of santonin in the presence of palladium black yields a dihydrosantonin and a tetra-hydrosantonin. The alcoholic solution of santonin containing palladium black is treated with hydrogen at 40—50 cm. pressure until the volume corresponding with the dihydro-compound has been absorbed (for 5 grams this takes fifteen to twenty minutes). The *dihydrosantonin*, $C_{15}H_{20}O_3$, so obtained, has m. p. 148—150°, $[a]_D + 23°$ (in 2·106% alcoholic solution), and gives with alcoholic potassium hydroxide a yellow solution having a green fluorescence. It yields a *semicarbazone*, $C_{16}H_{23}O_3N_3$, which forms microscopic needles, m. p. 238—239°.

When the hydrogenation is continued until a further equal amount of hydrogen has been absorbed, a *tetrahydrosantonin*, $C_{15}H_{22}O_3$, is obtained; it forms colourless laminæ, m. p. 154—155°, $[a]_D + 61\cdot5°$ (in 2·234% alcoholic solution). This substance does not become yellow when exposed to light, and is stable towards permanganate; it yields no coloration with potassium hydroxide.   R. V. S.

Combination of Phenolcarboxylic Acids. III. FERDINAND MAUTHNER (*J. pr. Chem.*, 1913, [ii], 87, 409—415).—A continuation of previous work (A., 1911, i, 725; 1912, i, 267).

Methyl p-3:5-*dimethoxybenzoyloxybenzoate*, prepared by shaking an ethereal solution of 3:5-dimethoxybenzoyl chloride with methyl *p*-hydroxybenzoate dissolved in aqueous sodium hydroxide, crystallises in colourless needles, m. p. 91—92°. *Methyl* m-3:5-*dimethoxybenzoyloxybenzoate*, from methyl *m*-hydroxybenzoate, has m. p. 66—67°.

Methyl m-3:5-*dimethoxybenzoyloxy*-p-*methoxybenzoate*, from 3:5-dimethoxybenzoyl chloride and methyl vanillate, has m. p. 89—90°.

Methyl 2-(3′:5′)-*dimethoxybenzoyloxy*-3-*naphthoate*, from methyl 2-hydroxy-3-naphthoate, has m. p. 119—120°.

3:4:5-Trimethoxybenzoyl chloride reacts with methyl *m*-hydroxybenzoate, yielding *methyl* m-3:4:5-*trimethoxybenzoyloxybenzoate*, m. p. 143—144°, and with methyl 2-hydroxy-3-naphthoate to form *methyl* 2-(3′:4′:5′)-*trimethoxybenzoyloxy*-3-*naphthoate*, m. p. 149—150°.

Methyl m-4-*methoxybenzoyloxybenzoate*, prepared from anisoyl chloride and methyl *m*-hydroxybenzoate, has m. p. 79—80°.

All the compounds described above crystallise in colourless needles.

The 3:4:5:2′:6′-pentamethyl ether of dimethyl gallate (A., 1911, i, 725) has m. p. 173—174°.   F. B.

Tetra-alkylation of *cyclo*Hexanone and β-Methyl*cyclo*hexanone and Trialkylation of Menthone. ALBIN HALLER (*Compt. rend.*, 1913, 156, 1199—1206. Compare A., 1908, i, 987; 1909, i, 108, 654; 1910, i, 219, 300; 1912, i, 269).—By the use of sodamide as condensing agent, all the hydrogen atoms attached to the two carbon atoms adjacent to the ketone group in the substituted or non-substituted *cyclo*hexanones can be substituted by alkyl groups, chiefly methyl and allyl, condensation of the *cyclo*hexanone on itself taking place to a certain extent at the same time. This latter condensation is increased if the methyl iodide is replaced by its higher homologues for substitution. The tetra-, penta-, and hexa-alkyl*cyclo*hexanones so obtained give neither oximes nor semicarbazones. The substitution is performed by dissolving the ketone (1 mol.) in anhydrous ether, or preferably toluene in some cases, adding the sodamide (1 mol.) in fine powder, and when all action has ceased adding the alkyl iodide in theoretical quantity. On the crude product obtained by treatment with water and then drying, this treatment is repeated two or three times. By this means the following compounds have been prepared:

1:1:3:3-*Tetramethylcyclohexan-2-one*, $CH_2\!\!<^{CH_2\cdot CMe_2}_{CH_2\cdot CMe_2}\!\!>CO$, b. p. 185—186°, $D^{17\cdot5}$ 0·8936, n_D^{18} 1·447, which on reduction with sodium

and alcohol gives the corresponding *alcohol*, b. p. 195—197°/767 mm., D^{17} 0·9001, n_D^{17} 1·455, giving a *phenylurethane*, m. p. 97—98°.

Attempts to prepare the ethyl derivatives by similar methods gave a mixture of small quantities of mono- and di-ethyl derivatives and a large amount of other condensation products.

1 : 1 : 3 : 3 - *Tetra-allylcyclohexan-2-one*, b. p. 170—171°/18 mm., D^{17} 0·9490, n_D^{16} 1·4920, giving on reduction the secondary *alcohol*, b. p. 171—173°/15 mm., D^{15} 0·9523, n_D^{17} 1·4975, which gave no phenylurethane.

1 : 2 : 2 : 4 : 4-Pentamethyl*cyclo*hexan-3-one (compare A., 1905, i, 214, 602) was prepared in an active and inactive form. The active ketone had b. p. 201—202°/765 mm., 93—94°/23 mm., D^{20} 0·8979, $n_D^{17·5}$ 1·4515, $[a]_D$ +24°0′, and gave the corresponding *alcohol*, b. p. 210—212°/767 mm., giving a *phenylurethane*, m. p. 105—106°. The inactive ketone had b. p. 202—203°/765 mm., D^{18} 0·8997, $n_D^{17·5}$ 1·4553, and gave the *alcohol*, m. p. 45°, b. p. 213—214°/767 mm., yielding a *phenylurethane*, m. p. 127°.

1-*Methyl*-2 : 2 : 4 : 4-*tetra-allyl*cyclo*hexan-3-one*, b. p. 165—169°/12 mm., D^{15} 0 954, $[a]_D$ +36°17′, on reduction yields the corresponding *alcohol*, b. p. 187—189°/25 mm., D^{17} 0·9613, $n_D^{16·5}$ 1·5054, $[a]_D$ -9°52′, which yields no phenylurethane.

The alkylation of the menthones in order to pass beyond the mono-alkyl stage had to be carried out in toluene as a solvent. The products so obtained were :

Dimethylmenthone, b. p. 108—109°/14 mm., which on reduction gave the *alcohol*, b. p. 245—247°, $[a]_D$ +3°23′, yielding a *phenylurethane*, m. p. 90—91°. Attempts to prepare trimethylmenthone were not successful.

Diallylmenthone has b. p. 146—147°/13 mm., $[a]_D$ +25°50′.

Triallylmenthone has b. p. 166—167°/14 mm., $[a]_D$ +6°40′.   W. G.

Arylsulphonylacetones, Arylsulphonylacetophenones, and Cyanobenzylarylsulphones. Julius Troger and O. Beck (*J. pr. Chem.*, 1913, [ii], 87, 289—311. Compare this vol., i, 169).—A number of arylsulphonylacetophenones, $SO_2R·CH_2·COPh$, and aryl-sulphonylacetones, $SO_2R·CH_2·COMe$, have been prepared by the inter-action of the sodium salts of arylsulphinic acids with ω-chloro-acetophenone and chloroacetone respectively. They resemble the aryl-sulphonylacetonitriles described previously (A., 1905, i, 336, 870), in that they dissolve in aqueous alkali hydroxides, and are reprecipitated un-changed by mineral acids. The mobility of the methylene hydrogen atoms in the arylsulphonyl-ketones is, however, not so great as in the case of the arylsulphonylacetonitriles, since condensation products with amyl nitrite and aromatic aldehydes could not be obtained.

Attempts to prepare arylsulphonylacetophenones by the action of magnesium phenyl bromide on the corresponding arylsulphonyl-acetonitriles proved unsuccessful, the latter compounds being recovered from the reaction unchanged. Acetonitrile and phenylacetonitrile readily react with magnesium phenyl bromide, yielding acetophenone and deoxybenzoin respectively. In the case of chloroacetonitrile, which should give rise to ω-chloroacetophenone, no definite compound

could be isolated from the reaction product. A similar retarding influence of the arylsulphonyl group has been observed with the arylsulphonylacetophenones, which do not react with organo-magnesium compounds, whereas acetophenone readily reacts with magnesium phenyl bromide and magnesium methyl iodide, yielding diphenyl-methylcarbinol and phenyldimethylcarbinol respectively.

o-*Methoxybenzenesulphonylacetone*, OMe·C_6H_4·SO_2·CH_2·COMe, prepared by heating sodium o-methoxybenzenesulphinate with chloroacetone in alcoholic solution, forms white, prismatic needles, m. p. 65°, and yields an *oxime*, m. p. 160·5°.

p-*Ethoxybenzenesulphonylacetophenone*, obtained from sodium p-ethoxybenzenesulphinate in a similar manner, crystallises in white needles, m. p. 67·5°; the *oxime* forms leaflets, m. p. 127°. The following compounds were prepared by heating ω-chloroacetophenone with the sodium salts of arylsulphinic acids in alcoholic solution: *benzenesulphonylacetophenone*, SO_2Ph·CH_2·COPh, which crystallises in white needles, m. p. 96°, and forms an *oxime*, m. p. 134°, a *semicarbazone*, m. p. 194·5°, and a *phenylhydrazone*, yellow needles, m. p. 170°; p-*chlorobenzenesulphonylacetophenone*, white needles, m. p. 132—133° (*oxime*, m. p. 131—132°), a-*naphthalenesulphonylacetophenone* forms white needles, m. p. 89°, and yields an *oxime*, m. p. 173°, and a *phenylhydrazone*, yellow, prismatic columns, m. p. 191—192°; p-*toluenesulphonylacetophenone*, m. p. 110° (*semicarbazone*, m. p. 208·5°); o-*methoxybenzenesulphonylacetophenone* forms stout, prismatic crystals, m. p. 79°, and yields a *phenylhydrazone*, crystallising in yellow prisms, which become yellowish-red at 165°, m. p. 167·5°; p-*ethoxybenzenesulphonylacetophenone*, white, prismatic needles, m. p. 130° (*oxime*, m. p. 150°).

ω-*Benzenesulphonyl*-p-*toluonitrile*, SO_2Ph·CH_2·C_6H_4·CN, obtained by the interaction of ω-chloro-p-toluonitrile and sodium benzenesulphinate in alcoholic solution, crystallises in white needles, m. p. 204·5°. The following sulphones were prepared in a similar manner: ω-p-*chlorobenzenesulphonyl*-p-*toluonitrile*, m. p. 148·5°; ω-p-*toluenesulphonyl*-p-*toluonitrile*, prismatic needles, m. p. 211°; ω-a-*naphthalenesulphonyl*-p-*toluonitrile*, m. p. 162·5°; o-*methoxybenzenesulphonyl*-p-*toluonitrile*, m. p. 121°; ω-p-*ethoxybenzenesulphonyl*-p-*toluonitrile*, m. p. 164°. The above-mentioned sulphones differ from the arylsulphonyl-ketones and nitriles in being insoluble in aqueous alkali hydroxides.   F. B.

The Friedel-Crafts Reaction. VI. GUSTAV HELLER (*Ber.*, 1913, **46**, 1497—1504. Compare A., 1912, i, 357, 358; etc.).—It has already been shown (A., 1912, i, 358; 1908, i, 994) that, whereas, o- and p-chlorotoluenes react normally with phthalic anhydride in the presence of aluminium chloride, the three bromotoluenes behave anomalously, yielding the same o-bromotoluoylbenzoic acid. The behaviour of the chloro- and bromo-toluenes with benzoyl chloride and aluminium chloride has therefore now been investigated.

[With LEOPOLD BUB.]—Benzoyl chloride was introduced into a well cooled mixture of o chlorotoluene and aluminium chloride, and the mixture subsequently warmed; the product was a *phenyl chlorotolyl ketone*, C_6H_3MeCl·COPh, colourless leaflets, m. p. 82—83°, which

was oxidised by chromium trioxide in acetic acid solution to a *chlorobenzophenonecarboxylic acid*, leaflets, m. p. indistinct at 187°. In a similar manner *p*-chlorotoluene gave rise to an isomeric *phenyl chlorotolyl ketone*, m. p. 35—36°, by the oxidation of which no characteristic acid could be obtained.

p-Bromotoluene, as also the *m*-isomeride, again exhibit anomalous behaviour, producing under similar conditions to the above only uncrystallisable oils, which from their inconstant b. p. must be mixtures caused probably by a wandering of the substituent groups during the reaction. On the other hand, *o*-bromotoluene gave an oily product which partly crystallised to a yellow solid, m. p. 173°, a *phenyl hydroxytolyl ketone*, $OH \cdot C_6H_3Me \cdot COPh$; this is the first case of the replacement of bromine by hydroxyl in a Friedel-Crafts reaction, and as the primary reaction occurred in the absence of water, the hydroxy-compound must have been produced from an intermediate substance during the subsequent treatment.

The interaction of phenol, aluminium chloride, and benzoyl chloride yielded a mixture of 4-hydroxydiphenyl-ketone and phenyl benzoate. *o*-Cresol gave the same phenyl hydroxytolyl ketone (*acetyl* derivative, needles, m. p. 68—69°) as was obtained in the above reaction with *o*-bromotoluene. *m*-Cresol produced a yellow oil, from which could be separated two isomeric *phenyl hydroxytolyl ketones*, yellow crystals, m. p. 63°, and colourless needles, m. p. 129° (compare Bartolotti, A., 1901, i, 36), respectively, and *m*-tolyl benzoate. The product obtained with *p*-cresol was exclusively *p*-tolyl benzoate.

It has already been shown that phthalic anhydride condenses with β-chloronaphthalene in the presence of aluminium chloride with the formation of an acid, which by dehydration gives a ketone (Heller and Grunthal, A., 1912, i, 357). Oxidation of the ketone by a mixture of potassium permanganate and nitric acid yielded anthraquinone-2 : 3-dicarboxylic acid; the ketone must therefore be of the structure

2-chloro-6 : 7-phthaloylnaphthalene, $C_6H_4 {<} {\overset{CO}{\underset{CO}{}}} {>} C_{10}H_5Cl$, and the acid must be an *o*-β-chloronaphthoylbenzoic acid, $C_{10}H_6Cl \cdot CO \cdot C_6H_4 \cdot CO_2H$.

D. F. T.

The Condensation of 2 : 5-Dimethoxybenzoyl Chloride with Phenolic Ethers. FERDINAND MAUTHNER (*J. pr. Chem.*, 1913, [ii], **87**, 403—409).—An account of the preparation of a number of methoxybenzophenones from 2 : 5-dimethoxybenzoyl chloride and phenolic ethers by means of the Friedel-Crafts reaction.

2 : 5-Dimethoxybenzoic acid is best prepared by methylating *o*-resorcylic acid with methyl sulphate and aqueous sodium hydroxide at the ordinary temperature; the chloride has b. p. 157—158°/16 mm., m. p. 35—36° (compare Kostanecki and Lampe, A., 1908, i, 442); the *amide* and *anilide* crystallise in lustrous, silky needles, m. p. 148—149° and 124—125° respectively.

3 : 5 : 4'-*Trimethoxybenzophenone*, prepared from the chloride and anisole in carbon disulphide solution in the presence of aluminium chloride, forms colourless needles, m. p. 97—98°.

3 : 5 : 3′ : 4′-*Tetramethoxybenzophenone*, obtained from veratrole in a similar manner, crystallises in colourless needles, m. p. 114—115°.

3 : 5 : 2′ : 4′-*Tetramethoxybenzophenone*, from resorcinol dimethyl ether, forms needles, m. p. 73—74°.

2′-*Hydroxy*-3 : 5 : 3′ : 4′-*tetramethoxybenzophenone*, prepared from pyrogallol trimethyl ether, forms light yellow crystals, m. p. 123—124°.

3 : 5 : 2′ : 4′ : 6′-*Pentamethoxybenzophenone*, from phloroglucinol trimethyl ether, crystallises in small needles, m. p. 132—133°.   F. B.

Benzilbenzoin. ALFRED BENRATH (*J. pr. Chem.*, 1913, [ii], **87**, 416—422).—Klinger's benzilbenzoin (A., 1886, 888) is produced by the photochemical reduction of benzil in solutions of aldehydes and aromatic hydrocarbons (compare Benrath, A., 1906, i, 535). When heated alone or in solution it decomposes into benzoin and benzil. Owing to this decomposition it has no definite m. p. ; it begins to soften at 86°, and is completely fused at a temperature dependent on the rate of heating, the highest recorded temperature being 143°. A mixture of benzil and benzoin in equimolecular proportions shows the same m. p. interval as benzilbenzoin, and hence the latter compound must have the formula COPh·COPh,COPh·CHPh·OH.

The fusion curve of mixtures of benzoin and benzil is recorded ; it shows a eutectic point at 86°.   F. B.

Preparation of Derivatives of *p*-Benzoquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 257834).—When *p*-benzoquinone, its homologues, or halogen derivatives are boiled with naphthylaminesulphonic acids in the presence of sodium acetate they yield compounds which, after further condensation with zinc chloride (or concentrated sulphuric acid), dye wood or silk in reddish-violet to blue shades.

The tinctorial properties of the *disulphonaphthylaminodichlorobenzoquinones* thus obtained from chloroanil with β-naphthylamine-5- and -8-sulphonic acids are tabulated in the original.   F. M. G. M.

Preparation of a Derivative of Anthraquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R-P. 258439).—When 1-aminoanthraquinone (10 parts) dissolved in 500 parts of cooled 60% sulphuric acid is slowly treated with sodium chlorate (2 parts) dissolved in 40 parts of the same solvent, a blue coloration is rapidly developed, followed by the separation of a deep blue precipitate which can be purified by boiling with alcohol and crystallisation from nitrobenzene.

This *compound* is not apparently obtained when other oxidising agents are employed; it gives a colourless "vat" with alkaline hyposulphite, and on further reduction with stannous chloride furnishes leucoquinizarin.   F. M. G. M.

Behaviour of Dibenzoyl-1 : 5-dibenzylaminoanthraquinone with Alkaline Sodium Hyposulphite. CHRISTIAN SEER (*Monatsh.*, 1913, **34**, 579).—A correction; dibenzoyl-1 : 5-dibenzylaminoanthraquinone is not reduced by alkaline hyposulphite as previously stated (A., 1912, i, 571).   D. F. T.

Preparation of Di- and Tri-anthrimides of the β-Anthra-quinone Series. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 257811).—It is found that dianthrimide can be prepared by heating together β-aminoanthraquinone (22·3 parts), β-chloroanthra-quinone (24·2 parts), and potassium carbonate (7 parts) at 300°, whilst trianthrimide, a brown powder, is obtained in a similar manner from 2 : 6-diaminoanthraquinone (1 mol.) and β-chloroanthraquinone (2 mols.) or from β-aminoanthraquinone and 2 : 7-dichloroanthraquinone.

F. M. G. M.
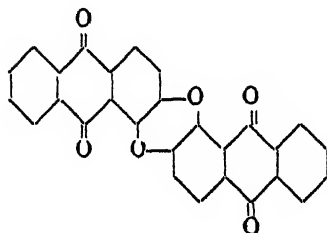
[**Preparation of an Anthra-quinone Derivative.**] R. WEDEKIND & Co. (D.R.-P. 257832).—The com-pound (annexed formula) is obtained by the condensation of 1-chloro-2-hydroxyanthraquinone; it crystallises from nitrobenzene, does not melt at 300°, and furnishes cotton dyes.

F. M. G. M.

Attempts to Prepare a 3 : 4 : 3′ : 4′-Tetrahydroxy-1 : 1′-di-anthraquinonyl. CHRISTIAN SEER and KARL EHRENREICH (Monatsh., 1913, 34, 631—648).—An unsuccessful endeavour to prepare a tetra-hydroxyanthraquinonyl with the hydroxyl groups disposed in the same positions as in alizarin (compare Scholl and Seer, A., 1911, i, 453).

4-Aminoalizarin proved useless as a starting point, as it was found impossible to convert this through the diazo-compound into 4-iodo-alizarin.

Alizarin dimethyl ether (1 : 2-dimethoxyanthraquinone) can be nitrated at 0° by potassium nitrate and sulphuric acid, or by nitric acid (D 1·51), with the formation of 4-nitro-1 : 2-dimethoxyanthra-quinone, deep yellow, prismatic needles, which give a red solution in sulphuric acid. This substance when suspended in aqueous ammonium sulphide at 100° is reduced to 4-amino-1 : 2-dimethoxyanthraquinone, deep red needles, m. p. 182—185°, the hydrochloride of which, after diazotisation in acetic acid and treatment with aqueous potassium iodide solution, is converted into 4-iodo-1 : 2-dimethoxyanthraquinone, yellowish-brown, prismatic needles, m. p. 172—174°. The position of the iodo-group in this, and therefore of the nitro group in the earlier substance, is proved by its red solution in sulphuric acid changing to a deep green (due to the formation of 3 : 4 : 3′ : 4′-tetramethoxy-μ-benzo-dianthrone, $CO\left\langle\begin{array}{c}C_6H(OMe)_2\\ C_6H_4\end{array}\right\rangle C=C\left\langle\begin{array}{c}C_6H(OMe)_2\\ C_6H_4\end{array}\right\rangle CO$; compare Scholl and Mansfeld, A., 1910, i, 494) when treated with copper powder. Attempts to achieve the desired aim of the research by heating the iodo-compound with aluminium chloride at 150—160° eliminated only two methoxy-groups with the formation of 4 : 4′ di-hydroxy-3 : 3′-dimethoxy-1 : 1′-dianthraquinonyl,

$C_6H_4\left\langle\begin{array}{c}CO\\ CO\end{array}\right\rangle C_6H(OH)(OMe)—C_6H(OH)(OMe)\left\langle\begin{array}{c}CO\\ CO\end{array}\right\rangle C_6H_4,$
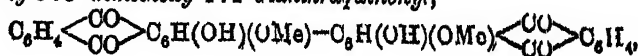
microscopic, orange-red prisms, which sublimes above 320°; it dissolves in alkali to a bluish-violet colour, which changes to red on addition of sodium hyposulphite.

Another attempt to achieve the object of the investigation was made by Scholl and Seer's method with phthalic anhydride (*loc. cit.*). For this purpose veratrole was nitrated to 4-nitro-1 : 2-dimethoxy-benzene, and this was reduced by tin and hydrochloric acid. Reduction at water-bath temperature produced, however, a halogen-substituted amino-compound, 2(?)-*chloro*-4 : 5-*dimethoxyaniline*, colourless needles, m. p. 72—73°; *hydrochloride*, needles, which slowly decompose above 150°; this was converted by diazotisation and potassium iodide into 2(?)-*chloro*-1-*iodo*-4 : 5-*dimethoxybenzene*, colourless needles, m. p. 69—70°, which, on heating with copper powder at 270—280° in an atmosphere of carbon dioxide, was converted into 6(?) : 6′(?)-*dichloro*-3 : 4 : 3′ : 4′-*tetramethoxydiphenyl*, colourless needles, m. p. 160—161°, soluble in sulphuric acid to a green solution. The successful reduction of nitrodimethoxybenzene to 4 : 5-dimethoxyaniline could be effected by the gradual addition of tin to the suspension of the solid in hydrochloric acid, and the product could then be converted into 1-iodo-4 : 5-dimethoxybenzene, but it was found that this substance can be more conveniently obtained by the action of iodine and mercuric oxide on an alcoholic solution of veratrole at the ordinary temperature. When heated with copper powder at 260°, the iodo-compound is converted into 3 : 4 : 3′ : 4′-*tetramethoxydiphenyl*, colourless, silky needles, m. p. 130—132°, the solution of which in sulphuric acid passes slowly from golden-yellow to emerald-green. It was not found possible to prepare from the last substance a tetrahydroxydianthraquinonyl of the desired structure; heating with phthalic anhydride and aluminium chloride yielded a complex, deep blue mixture in which the desired substance was probably present. D. F. T

Camphor and Phenols. I. Compounds of Camphor with Quinol, Resorcinol, and Catechol. N. N. Efremov (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 348—362).—Thermal and micrographic examination of mixtures of camphor with the three dihydroxybenzenes demonstrates the existence of the three isomeric compounds,

$$C_6H_4(OH)_2, C_{10}H_{16}O,$$
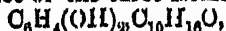
melting without decomposition at 29·0° (ortho) and 11·5° (meta) respectively. The compound with quinol also melts without decomposing, but it does not correspond with a maximum on the melting-point curve.

The dihydroxybenzenes form with camphor solid solutions containing for resorcinol, 20·0%, for catechol, 15%, and for quinol, 37·5% by weight of camphor.

The eutectic mixtures formed by camphor with the dihydroxybenzenes are viscous liquids prone to supercooling, and crystallise slowly only at −15° to −20° in spherolites having a fine granular structure. In each case the eutectic mixture contains 66·6 mols.% of camphor and has a characteristic yellow colour. T. H. P.

The Constitution of "Terpineol-35°-glycuronic Acid." Juno Hamalainen (*Biochem. Zeitsch.*, 1913, **50**, 220—222).—The conjugation

of the terpineol with glycuronic acid takes place with the scission of
water. The author has administered the alcohol to rabbits, and
succeeded in isolating the acid from the urine in the form of the
anhydrous sodium salt, $C_{16}H_{25}O_7Na$. The urine was first precipitated
with normal and then with basic lead acetate. The precipitate from
the latter contained the lead salt of the glycuronate ; from this the
barium salt was obtained, and was crystallised from a water-alcohol-
ether mixture. By treatment of this with the theoretical amount of
sodium sulphate, a crystalline hydrated sodium salt was prepared.

<div align="right">S. B. S.</div>

Essential Oil of Crithmum maritimum (Linn.) from Sardinia.
LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v],
22, i, 231—237, 312—317).—The oil of this plant from Sardinia
differs from that from a French source described by Delépine, A., 1909,
i, 642 ; 1910, i, 401).—Details are given of the properties of various
fractions of the oil and of the yield from different parts of the plant.
The chemical investigation of the oil shows that the only constituents
common to both are dillapiole and *p*-cymene. The *d*-pinene, dipentene,
and thymol methyl ether of the French oil are not present in the
other, which contains, however, β-phellandrene and a new terpene, to
which the name *crithmene* is applied. There is also a white *substance*
crystallising in leaflets, m. p. 63°, which has the properties of a paraffin.
Crithmene yields an *a-nitrosochloride*, which crystallises in laminæ,
m. p. 101—102°, and a β-nitrosochloride, $C_{10}H_{16}ONCl$, which forms
quadratic plates, m. p. 103—104° ; both are optically inactive. The
tetrabromide is oily. The *nitrolpiperides* prepared from the nitroso-
chlorides have m. p. 138°. The compound with *benzylamine* has m. p.
103—104°. When the nitrosochloride is decomposed with alcoholic
potassium hydroxide and distilled in steam, a white, micro-crystalline
substance, m. p. 131°, is left ; it contains nitrogen, and when heated
with hydrochloric acid does not reduce Fehling's solution. When the
decomposition of the nitrosochloride is effected under somewhat
different conditions, a yellow, stable, crystalline *substance*, m. p.
53—54°, is obtained. The fractions of the oil, b. p. 178--179°, gave a
crystalline *nitrosite*, m. p. 89—90°. The new terpene yields a dihydro-
chloride, m. p. 52°, identical with that of terpinene.   R. V. S.

Constitutional Formula of Orithmene.   III. LUIGI
FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad.
Lincei*, 1913, [v], 22, i, 382—386. Compare pre-
ceding abstract).—After reviewing the various formulæ
possible for this substance, the authors believe it to
be $\Delta^{1,7-4,8}$-p-*menthadiene* (annexed formula),
This constitution accords with the physical and
chemical properties of the substance.   R. V. S.

Depolymerisation and Transformation of Caoutchouc. G.
STAFFORD WHITBY (*Zeitsch. Chem. Ind. Kolloids*, 1913, 12, 190—193.
Compare this vol., i, 575).—It has been found that certain samples of

caoutchouc undergo a form of degenerative change in which the caoutchouc is converted into resin. During this process the original "tackiness" of the caoutchouc disappears, and the samples assume a smooth, polished appearance and become brittle. The extent to which the transformation occurs may be seen by the fact that a sample of such caoutchouc, which gave 9·9% of resin six weeks after collection, was found to contain 78% at the end of sixteen weeks.

The transformation is accompanied by increase in weight as a result of oxidation. A sample containing 19% of resin was found to have increased in weight to the extent of 4·38% at the end of three weeks. When kept in an air-bath at 100°, the increase in weight during the same period was 1·63%. The change goes on therefore at 100°, but at a slower rate. It is shown that the degenerative process has no connexion with the action of light, and that it is probably due to abnormal conditions, the origin of which must be sought for in the living plant. In this connexion, the function of the latex in the plant is obviously of primary importance, and in the later part of the paper the author puts forward the view that the latex represents a reserve supply of food which is rendered available by the action of an oxydase, and that the degenerative change of the extracted latex bears some relation to this oxidation process. H. M. D.

Chemistry of Caoutchouc. III. Additive Compounds of Caoutchouc with Halogen Hydracids and Halogens. Friedrich W. Hinrichsen, Hermann Quensell and Erich Kindscher (*Ber.*, 1913, **46**, 1283—1287).—Attempts have been made to obtain non-colloidal derivatives from caoutchouc, but without success. Cold benzene or chloroform solutions of pure Para caoutchouc have been saturated with hydrogen chloride, bromide or iodide, but the substances obtained on dilution with light petroleum still showed the Brownian movement when viewed in benzene solution under the ultra-microscope. The analyses were somewhat low for the *dihydrochloride*, $C_{10}H_{16},2HCl$, a white powder, and the *dihydrobromide*, a white powder, which still retained bromine after boiling with alcoholic potassium hydroxide, whilst the *hydriodide*, $C_{10}H_{16},HI$, was a colourless, sticky substance.

Chlorine in cold chloroform gave rise to substitution as well as addition, a white *powder*, which after repeated precipitation from alcohol gave numbers approximating to the formula $C_{10}H_{11}Cl_6$ (compare Gladstone and Hibbert, T., 1888, **53**, 679). The bromination of caoutchouc in ice-cold chloroform is practically independent of the amount of bromine used or of the time, and leads to the tetrabromide. The application of the process to the estimation of caoutchouc will be published later. J. C. W.

Chemistry of Caoutchouc. IV. Action of Iodine on Caoutchouc. Friedrich W. Hinrichsen and Richard Kempf (*Ber.*, 1913, **46**, 1287—1291).—Weber (A., 1900, i, 354) described a compound, $C_{20}H_8I_6$, which he obtained by the action of iodine on caoutchouc in cold chloroform. Such a great absorption of iodine could not be obtained in the present experiments, but it is found that

the process is a photochemical reaction, and, as such, is almost independent of temperature. Small portions of a 1% solution of iodine were quickly rendered colourless in sunlight on addition to a 1% solution of caoutchouc in carbon disulphide, when the end-point corresponded with the absorption of one atom of iodine by two molecules of hydrocarbon. A specific action of short-waved light could not be determined, but the volume of air over the liquid seemed to be of importance. On filtering the bleached and somewhat evaporated solution into light petroleum, a white *powder* was obtained which approximated to the formula $C_{20}H_{27}O_7I$. It gave up iodine when kept, but in an iodine atmosphere in the dark it rapidly absorbed the halogen, and after three weeks had increased in weight by 170%. The glistening black *product* approximated therefore to $C_{20}H_{27}O_7I_8$.   J. C. W.

Chemistry of Caoutchouc. V. Treatment of Caoutchouc with Sulphur Chloride and Sulphur. FRIEDRICH W. HINRICHSEN and ERICH KINDSCHER (*Ber.*, 1913, **46**, 1291—1297. Compare A., 1910, i, 330).—The cold vulcanisation of caoutchouc was studied by mixing a constant weight of caoutchouc in dry benzene with varying amounts of sulphur chloride and, after some time, measuring the excess of reagent. The end-product was found to agree with the formula $(C_{10}H_{16})_2S_2Cl_2$. The action of sulphur was first studied in naphthalene solution, but now systematic experiments have been carried out at 170° in cumene. The product is repeatedly extracted with acetone, when the resulting hard, brown powder is found to contain a proportion of sulphur which approaches to 32% more and more as the initial concentration of sulphur and the time of heating are increased. This corresponds with $C_{10}H_{16}S_2$ (compare Spence and Young, A., 1912, i, 706), and since the substance does not absorb bromine it is regarded as a definite compound. If the uncombined sulphur is extracted by alcoholic sodium hydroxide, however, the product contains less than 26% of sulphur.   J. C. W.

Vulcanisation of Caoutchouc. II. GUSTAV BERNSTEIN (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 193—196. Compare A., 1912, i, 1006).—The "depolymerisation" of caoutchouc under the influence of a rise of temperature, mechanical treatment, and ultra-violet light has been investigated by measurements of the viscosity of xylene solutions of the caoutchouc. Samples of caoutchouc which in xylene solution show widely different viscosities are found to give the same value for the viscosity when subjected to the depolymerising action of heat, light or mechanical treatment until the viscosity has become constant. This result would seem to show that the state of aggregation which is finally attained is independent of the special characteristics of the original caoutchouc.

From measurements of the viscosity of xylene solutions of Hevea Plantation caoutchouc which was heated for five hours at temperatures between 30° and 100°, it has been found that rapid depolymerisation begins at 60—70°. This temperature was found to vary somewhat when caoutchoucs from other sources were examined in the same way.

If sulphur is mixed with the caoutchouc before exposure to ultraviolet light, it is found that vulcanisation takes place as a result of the light treatment. Vulcanisation also occurs when a xylene solution containing caoutchouc and sulphur is exposed to the short-waved rays.

H. M. D.

Synthetic β-Glucosides of the Terpene Alcohols. Juho HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1913, **50**, 209—219).—By the method already described (this vol., i, 497), the following substances were prepared. *Sabinol-tetra-acetyl*-d-*glucoside*, $C_{24}H_{34}O_{16}$, long, glistening needles, m. p. 121° (corr.). *Sabinol-glucoside*, $C_{16}H_{26}O_6,H_2O$, m. p. 65—68° (corr.), $[a]_D^{20}$ of anhydrous substance − 33·60°. This glucoside is hydrolysed by emulsin. d-*Camphenilol-tetra-acetyl*-d-*glucoside*,

$$C_{23}H_{34}O_{10},$$

long, glistening needles, m. p. 128·5—130° (corr.). d-*Camphenilol*-d-*glucoside*, $C_{15}H_{26}O_6,H_2O$, m. p. 95—98° (corr.), $[a]_D^{20}$ of anhydrous substance − 25·47°. This is slowly hydrolysed by emulsin. l-*Fenchyl-tetra-acetyl*-d-*glucoside*, $C_{24}H_{36}O_{10}$, m. p. 119—121·5° (corr.). l-*Fenchyl*-d-*glucoside*, $C_{16}H_{28}O_6$, with $[a]_D^{20}$ − 36·57°. The substance with water of crystallisation has m. p. 124—127° (corr.), m. p. of anhydrous glucoside 130—132·5° (corr.), sinters at 122°. It is slowly hydrolysed by emulsin. r-*Borneol-tetra-acetyl*-d-*glucoside*, $C_{24}H_{80}O_{10}$, m. p. 119·5—122·5° (corr.). r-*Borneol*-d-*glucoside*, $C_{16}H_{28}O_6$, with $[a]_D^{20}$ − 32·99°, m. p. of substance with water of crystallisation 133—134·5° (corr.), and of anhydrous substance 143—144·5° (corr.), sinters at 132°. It is very slowly hydrolysed by emulsin. l-*Borneol-tetra-acetyl*-d-*glucoside*, $C_{24}H_{36}O_{10}$, m. p 124° (corr.). l-*Borneol*-d-*glucoside*, $C_{16}H_{28}O_6,H_2O$, m. p. 132·5—133·5° (corr.). The anhydrous substance has m. p. 138—141° (corr.), and $[a]_D^{20}$ − 60·12°. It is fairly readily hydrolysed by emulsin.

S. B. S.

Helleborein. ERNST SIEBURG (*Arch. Pharm.*, 1913, **251**, 154—183. Compare Thaeter, A., 1898, i, 39).—Helleborein is shown to belong to the group of saponins. On hydrolysis it yields acetic acid, dextrose, arabinose, and two sapogenins called "acid" and "neutral" helleboretin respectively, which are closely related and probably contain a terpene-like nucleus. As the result of pharmacological experiments, the author suggests that helleborein is not a suitable substitute for digitalin in medicine.

Helleborein (Merck), $(C_{21}H_{34}O_{10})_2$, $[a]_D^{20}$ − 2·8°, is amorphous; it furnishes an *acetyl* derivative, $(C_{21}H_{29}O_{10}Ac_5)_2$, m. p. 129—130°, which separates from alcohol in yellow scales, and on treatment with baryta yields a *product*, which is helleborein less one acetyl group (see below), and forms a pale yellow powder. *Benzoylhelleborein*, $(C_{21}H_{29}O_{10}Bz_5)_2$, m. p. 142°, is a snow-white, amorphous substance. When boiled with baryta solution, helleborein loses one molecule of acetic acid, and the latter acid is also formed when the glucoside is treated with bromine water. On hydrolysis, by boiling with dilute sulphuric acid, 1 mol. of acetic acid and 2 mols. each of dextrose and arabinose are formed. The other products of hydrolysis are *acid helleboretin* and *neutral helleboretin*. The former has the formula $C_{21}H_{86}O_7$, and appears to be a lactone, since it does not decompose carbonates and is not completely

soluble in alkali hydroxide solutions. Its behaviour on treatment with melted potassium hydroxide or nitric acid, and on distillation with zinc dust is recorded. Neutral helleboretin, $C_{15}H_{24}O_3$, is a greenish-black mass. The deacetylated helleborein referred to above does not produce hæmolysis, and is not poisonous to rabbits.   T. A. H.

Structure of the Natural Saponins. ANNE W. VAN DER HAAR (*Arch. Pharm.*, 1913, **251**, 217—222. Compare A., 1912, i, 885).— The method of investigation previously described (*loc. cit.*) has been applied to guaiacum-saponin, saponin and sapotoxin from Levantine saponaria root, senegin and digitonin, and it is shown that all five of these saponins give the characteristic colour reaction with sulphuric acid. Further, the sapogenins obtained from them by acid hydrolysis, on distillation with zinc dust, yield products which can be separated by steam distillation into terpene-like oils and non-volatile products. The terpene-like oils give a violet coloration with acetic acid and sulphuric acid, whilst the non-volatile substances give the blue (phytosterol) reaction with this reagent. In the case of the products from the sapogenin derived from senegin, these colour reactions are, however, reversed.   T. A. H.

Strophanthic Acid, a Saponin from the Seeds of Strophanthus Gratus. ERNST SIEBURG (*Ber. Deut. pharm. Ges.*, 1913, **23**, 278—290).—The different varieties of *Strophanthus* do not contain more than 0·2% of strophanthic acid.

The mother liquors obtained in the manufacture of *g*-strophanthin formed the starting material for the isolation of the acid. They were neutralised, diluted with water, freed from fat, and acidified with hydrochloric acid. The crude precipitated acid was repeatedly washed with water, and then precipitated with basic acid acetate; the precipitate was washed with water, and extracted with boiling 80% alcohol; the extract was diluted with water and shaken with *iso*butyl alcohol; from its solution in the latter medium, *g*-strophanthic acid was precipitated by addition of ether as a white, amorphous, voluminous mass, which was acid towards litmus, and readily dissolved in aqueous alkali carbonate and hydrogen carbonate solutions.

g-Strophanthic acid is precipitated from its aqueous solution by phosphotungstic, phosphomolybdic, and picric acids, but not by tannin. It has only feeble reducing action towards the ordinary reagents. It does not contain a methoxy-group. It yield precipitates with the salts of many heavy metals, such as copper, lead, zinc, ferrous and ferric iron, and barium, but the products do not appear to be definite chemical individuals. The solubility of the free acid appears to depend somewhat on the age of the specimens. Ultimate analysis, titration with sodium hydroxide, and analysis of the *silver* and *lithium* salts lead to the formula $C_{21}H_{34}O_{10}$ for the acid, but determination of molecular weight in glacial acetic acid solution indicates the formula $(C_{21}H_{34}O_{10})_4$.

When hydrolysed with 3% aqueous sulphuric acid, and subsequently with 4% alcoholic hydrochloric acid, strophanthic acid yields dextrose and *strophanthigenin*, $(C_{12}H_{18}O_2)_2,3\frac{1}{3}H_2O$, white needles, m. p. about

291°. The latter is faintly acidic in solution, but does not dissolve even in concentrated alkali. With bromine in glacial acetic acid solution, it yields an uncrystallisable *product*, $C_{12}H_{14}Br_2O_2$. Oxidation with potassium permanganate converts it into a crystalline *acid*, which has not been further investigated.

The following colour reactions are shown by *g*-strophanthic acid, and generally with greater readiness by *g*-strophanthigenin, but are not given by *k*-strophanthin, *g*-strophanthin, or *g*-strophanthidin : (1) a trace of substance gives an immediate yellowish-red coloration, with concentrated sulphuric acid, which gradually changes to an eosine-red with greenish fluorescence ; (2) if a dilute solution of the substance in alcohol is mixed with an alcoholic solution of benzaldehyde and evaporated, the residue gives an immediate bright red coloration with sulphuric acid ; (3) if a trace of the substance is dissolved in acetic anhydride and concentrated sulphuric acid cautiously added, a red ring is formed which rapidly becomes violet, then blue, and finally green ; (4) a saturated alcoholic solution of dextrose or arabinose yields with a trace of substance and concentrated sulphuric acid a red ring which quickly turns to violet ; with furfuraldehyde, under like conditions, a blue to green colour is developed ; (5) if rhamnose is used, as in (4), a permanent, deep cherry-red colour is formed ; (6) a solution of the substance in a mixture of nine parts trichloroacetic acid and one part concentrated hydrochloric acid gradually develops a pale violet colour, which becomes more intense and slightly fluorescent.　　　H. W.

Thiophen Analogues of Triphenylethyl. Moses Gomberg and R. L. Jickling (*J. Amer. Chem. Soc.*, 1913, **35**, 446—447).—Attempts have been made to prepare analogues of triphenylmethyl containing other than exclusively aromatic groups.

Thienyldiphenylcarbinyl chloride has m. p. 81° ; when a solution in benzene is treated with molecular silver, it becomes dark red, and an unsaturated hydrocarbon is produced which absorbs oxygen with formation of the peroxide $(C_4SH_3 \cdot CPh_2)O_2$.

Dithienylphenylcarbinol, m. p. 90°, has been prepared by the Grignard synthesis from ethyl benzoate and thienyl chloride.　E. G.

1 : 4-Dithiens. Treat B. Johnson, Robert C. Moran, and Edward F. Kohmann (*J. Amer. Chem. Soc*, 1913, **35**, 447—452).— Johnson and Moran (A., 1912, i, 913) have found that when 2-benzoyl-methylthiol-4-methyl-1 : 6-dihydro-6-pyrimidone is hydrolysed with concentrated hydrochloric acid, it yields 4-methyluracil together with a crystalline compound containing sulphur. A study of the latter compound has shown that it has the structure $S{<}^{CPh:CH}_{CH:CPh}{>}S$, and it has therefore been designated 2 : 5-diphenyl-1 : 4-dithien. Both this substance and the corresponding 2 : 5-ditolyl compound are yellow, but dissolve in concentrated sulphuric acid to form beautiful purple solutions. Characteristic colorations are also produced by strong nitric acid and by solution of bromine in glacial acetic acid. In this respect the dithiens resemble Fries and Volk's thianthren compounds (A., 1909, i, 406). 1 : 4-Dithien, the parent substance of the compounds now

described, has been obtained by Levi and termed by him biophon (A., 1891, 551).

2 : 5-*Diphenyl*-1 : 4-*dithien*, m. p. 118—119°, crystallises in yellow prisms and is exceedingly stable.

2-p-*Toluoylmethylthiol* 4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*,

$$NH \underset{CO \underline{\hspace{3.5cm}} OH}{\overset{C(S \cdot CH_2 \cdot CO \cdot C_6H_4Me):N}{<>}} CMe,$$
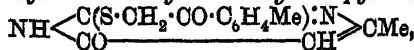
m. p. 194—195°, obtained by the action of p-chloroacetyltoluene on the sodium salt of 2-thio-4-methyluracil, forms colourless, prismatic crystals. On hydrolysis with 20% hydrochloric acid, it yields 2 : 5-*di-tolyl*-1 : 4-*dithien*, m. p. 137—138°, which crystallises in yellow needles.

E. G.

The Hellebore Group. III. Alkaloids of Delphinium Ajacis. OSKAR KELLER and O. VOLKER (*Arch. Pharm.*, 1913, **251**, 207—216. Compare A., 1910, ii, 887, 888).—This plant yields two new alkaloids, which are characterised.

The alkaloids were isolated from an alcoholic extract of the seeds. *Ajacine*, $C_{15}H_{21}O_4N,H_2O$, m. p. 142—143°, crystallises in colourless needles from dilute alcohol, is alkaline in reaction, and yields salts which are readily soluble and difficult to crystallise. The *hydrochloride*, $B_2,HCl,2H_2O$, m. p. 93°, is amorphous, as is also the *aurichloride*, $B_2,HAuCl_4$, and the *platinichloride*, B_4,H_2PtCl_6. The alkaloid absorbs bromine, contains 3 methoxyl groups, is not esterified by benzoyl chloride or acetic anhydride, does not react with methyl iodide or methyl sulphate, and is not affected by nitrous acid. On oxidation, it furnished a product smelling of butyric or valeric acid, and on distillation with zinc dust yielded a substance having an odour of benzaldehyde. On treatment with cyanogen bromide, it furnished a crystalline *compound*, m. p. 132—133°.

Ajaconine, m. p. 162—163°, forms colourless, glancing prisms, but concordant results could not be obtained on combustion, and crystalline salts could not be prepared. It contains no methoxyl groups. With methyl iodide, a crystalline *methiodide*, m. p. 121°, slender needles, was obtained, which appears to have the formula $C_{18}H_{31}O_2N,HI,H_2O$, whence the formula $C_{17}H_{29}O_2N$ is assigned provisionally to the parent base. The latter may be a secondary base, since it reacts with nitrous acid, forming a substance which gives Liebermann's reaction. Ajaconine also yields an amorphous *dibenzoyl* derivative, from which an amorphous *aurichloride* was prepared.

The behaviour of both alkaloids with the usual precipitants and reagents is described. The seeds also contain other alkaloids, which are amorphous.

T. A. H.

Comparative Solubility of Morphine and Narcotine in Pure or Aqueous Acetone and in Distilled Water. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1913, [vii], **7**, 438).—One litre of pure anhydrous acetone dissolves at 15°, 1·28 grams of morphine and 41·96 grams of narcotine. In a mixture of equal volumes of acetone and water at 15°, the solubilities are morphine 1·32 grams, and narcotine 0·70 gram

per litre. In distilled water at 15°, the solubilities are morphine, 0·288 gram, and narcotine, 0·10 gram per litre. W. P. S.

*apo*Morphine. I. Supposed Formation of *apo*Morphine on Heating or Keeping Morphine Solutions. MORITZ FEINBERG (*Zeitsch. physiol. Chem.*, 1913, **84**, 363—378).—*apo*Morphine is not formed either on prolonged boiling of morphine, morphine hydrochloride, or liquids containing morphine, such as pantopone, or on keeping such solutions with or without the addition of a nutrient substance. The separations occasionally observed from such solutions are due to traces of the sparingly soluble morphine base. Preparations of *apo*morphine obtained in commerce had the theoretical proportion of chlorine, and agreed as to their optical activity. They are therefore to be regarded as pure. E. F. A.

The Polymorphism of Codeine, Thebaine, and Narcotine; a New Type of Spherolites. PAUL GAUBERT (*Compt. rend.*, 1913, **156**, 1161—1163).—Codeine, thebaine and narcotine, and other alkaloids derived from opium, exhibit the phenomenon of superfusion, become solid without crystallisation, and can be kept in this vitreous state for several months. They are all polymorphic, codeine having five crystalline forms, narcotine three, and thebaine two, varying in stability with the temperature, and they also all present curious spherolitic formations at different temperatures. W. G.

The Structure of Ratanhine. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1913, **34**, 659—664. Compare this vol., i, 71).—The estimation of methyl attached to nitrogen in ratanhine indicates the presence of a methylamino-group in this substance, and it is therefore possible that ratanhine is α-methylamino-β-*p*-hydroxyphenylpropionic acid (methyltyrosine). The m. p. is so indefinite that it is of little use as a comparison with the synthetical substance of this structure (Johnson and Nicolet, A., 1912, i, 585), but the action of iodine on alkaline solutions of ratanhine and of the synthetic substance produces apparently the same di-iodo-compound from each. The probability of the above structure for ratanhine is strongly confirmed by the close resemblance of the base, which is obtained by scission of carbon dioxide, with β-*p*-hydroxyphenylethylmethylamine (Walpole, T., 1910, **97**, 945); the free bases, together with the hydrochlorides and platinichlorides, exhibit a close agreement in m. p. It is therefore to be accepted that ratanhine, which is also known by the names surinamine (Blau, A., 1909, i, 51), geoffroyine, angeline, and andirine, is α-methylamino-β-*p*-hydroxyphenylpropionic acid,

$$OH·C_6H_4·CH_2·CH(NHMe)·CO_2H.$$ D. F. T.

Synthesis of 2:3:4-Trimethylpyrrole and of 2:3:4-Trimethyl-5-ethylpyrrole (Isomeric Phyllopyrroles). HANS FISCHER and AMANDUS HAHN (*Zeitsch. physiol. Chem.*, 1913, **84**, 254—261).—Fischer and Krollpfeiffer (this vol., i, 93) have described the formation of the phthalide of a trimethylpyrrole by treating tetramethylpyrrole with phthalic anhydride. Potassium hydroxide

converts this phthalide into the corresponding acid, which after prolonged treatment with glacial acetic acid and hydrogen iodide lov the phthalic acid residue and forms 2 : 3 : 4-trimethylpyrrole, describet by Piloty and Hirsch (A., 1912, i, 925). This alkylpyrrole has marked crystallising properties; it forms a crystalline picrate and an azo-dye, and is oxidised by nitrous acid to an oxime, which is converted into dimethylmaleinimide on hydrolysis.

Heating with sodium ethoxide converts the trimethylpyrrole into the isomeric phyllopyrrole, which does not crystallise.

Tetramethylpyrrole is produced when the above phthalide is heated with sodium methoxide.

On heating indigotin with sodium methoxide in sealed tubes at 230°, the C:C-junction is broken, and dimethylindole is formed as well as a second unknown compound, which crystallises well and forms a picrate, m. p. 176—177°.

3 : 4 : 5-Trimethylpyrrole crystallises in prisms, m. p. 37—38°, becoming red when exposed to the air. The picrate has m. p. 147—148°.   E. F. A.

Complex Acetatoferri-bases Containing Pyridine. RUDOLF F. WEINLAND and CHR. BECK (*Zeitsch. anorg. Chem.*, 1913, **80**, 402—447. Compare A., 1910, i, 296, 635).—When pyridine (5 mols.) is added to a solution of hydrated ferric chloride (1 mol.) in glacial acetic acid (5 mols.), heat is developed and a dark green mass is obtained on cooling. When this is dissolved in chloroform and precipitated with benzene, yellowish-green crystals are obtained. Digestion with absolute alcohol converts this salt, with loss of water, into a brown, octahedral salt, and an exactly similar salt is obtained from ferric bromide. The original chloride yields a yellowish-green iodide with concentrated aqueous potassium iodide, the chlorine being completely eliminated, whilst the chloride is regenerated from the acetate and lithium chloride. These reactions point to the formulæ:

$$\mathrm{Fe_4} \begin{array}{c} (\mathrm{OAc})_6 \\ 3\mathrm{Py} \\ (\mathrm{OH})_2 \end{array} \Big] \mathrm{Cl_4} \quad \text{and} \quad \mathrm{Fe_4} \begin{array}{c} (\mathrm{OAc})_6 \\ 3\mathrm{Py} \\ \mathrm{O} \end{array} \Big] \mathrm{Cl_4}$$
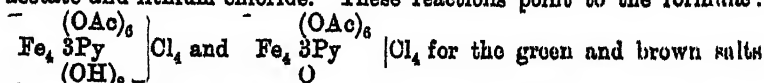
for the green and brown salts respectively. The original crude product is a chloride-acetate, containing more pyridine. The brown solutions of these salts in water slowly decompose, forming a gelatinous precipitate. Benzene does not precipitate a pure tetrabromide from chloroform solution, but a mixed salt containing more pyridine. Removal of water gives a salt corresponding exactly with the chloride.

A solution of ferric acetate and lithium iodide in glacial acetic acid yields an iodide-acetate, composed of two mixed salts. Digestion with absolute alcohol yields a red, octahedral periodide-acetate,

$$\mathrm{Fe_4} \begin{array}{c} (\mathrm{OAc})_6 \\ 4\mathrm{Py} \\ \mathrm{O} \end{array} \Big] \begin{array}{c} \mathrm{I_2 \cdot I_2} \\ (\mathrm{OAc})_2 \end{array}.$$
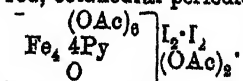
The iodide obtained from the chloride is a mixed salt. Nitrate acetates have also been obtained.

Ferric acetate, pyridine, and glacial acetic acid yield a compound,

$\text{Fe}_4 \begin{array}{l}(\text{OAc})_6 \\ 3\text{Py} \\ \text{OH}\end{array} \bigg| (\text{OAc})_6.$ Dissolving in chloroform and precipitating

with benzene gives a bright copper-red salt,

$$\text{Fe}_3 \begin{array}{l}(\text{OAc})_5 \\ \text{Py} \\ (\text{OH})_2\end{array} (\text{OAc})_2, \text{H}_2\text{O}.$$
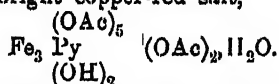
Solutions of ferric chloride in at least 15 mols. glacial acetic acid yield after a time with 2 mols. of pyridine, garnet-red prisms, which contain more chlorine than the previous salts, and appear to contain a complex anion, $\left[\text{Fe}\begin{array}{l}\text{Cl}_5 \\ \text{H}_2\text{O}\end{array}\right]^{-}$ which is already known. The salt is acid and is only stable in presence of an excess of acetic acid. It has the constitution $\text{Fe}_4 \begin{array}{l}(\text{OAc})_6 \\ 5\text{Py}\end{array}\left[\begin{array}{l}(\text{OAc})_2,\text{CH}_3\cdot\text{CO}_2\text{H} \\ \left[\text{Fe}\begin{array}{l}\text{Cl}_5 \\ \text{H}_2\text{O}\end{array}\right]_2\end{array}\right]$,12H$_2$O. It yields a periodide with concentrated aqueous potassium iodide,

$$\text{Fe}_4 \begin{array}{l}(\text{OAc})_6 \\ 5\text{Py} \\ \text{OH}\end{array} \begin{array}{l}\text{I}_3,\text{I}_3 \\ (\text{OAc})_2\end{array}.$$
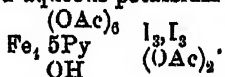
The iron atoms in the complex cations are regarded as linked together through the acetyl groups by means of subsidiary valencies. The pyridine in these compounds, like the ammonia in the complex chromiacetates, can pass in and out of the cation without, as in metal-ammines, affecting the negative groups.   C. H. D.

Pyridine Derivatives. ERNST SCHMIDT (*Arch. Pharm.*, 1913, **251**, 188—207).—In continuation of work already described (A., 1905, i, 23), attempts have been made to prepare formocholine (trimethylhydroxymethylammonium hydroxide), and in default of this its pyridine analogue, by new methods which will give larger yields. The products obtained in these unsuccessful attempts are described.

Prescott and Baer (A., 1897, i, 95) have shown that by the interaction of methylene iodide and pyridine, methylenedipyridyl iodide, $\text{CH}_2(\text{C}_5\text{H}_5\text{NI})_2$, is formed, and a further study of this reaction under various conditions shows that this is practically the sole product. It forms yellow leaflets, m. p. 220° (decomp.), but after decolorisation by animal charcoal forms colourless tablets, m. p. 222—223°, containing 1H$_2$O from water. The *chloride*,
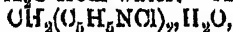
$$\text{CH}_2(\text{C}_5\text{H}_5\text{NCl})_2,\text{H}_2\text{O},$$

is similar, but remains unmelted at 260°. The *platinichloride* forms yellow needles from alcohol, and does not melt at 260°. The *picrate* forms long, yellow needles, m. p. 230°, and the *mercurichloride*, $\text{CH}_2(\text{C}_5\text{H}_5\text{NCl})_2,4\text{HgCl}_2$, long, glancing needles, m. p. 230°; the mother liquor from the preparation of the latter salt deposits on evaporation a second *mercurichloride*, m. p. 124—126°, containing 1 mol. HgCl$_2$.

Attempts to demethylate pyridylformocholine methyl ether (A., 1901, i, 443) by L. KRAUSS furnished only pyridine.

Re-examination of Prescott and Baer's work (*loc. cit.*) on the interaction of ethylene bromide and pyridine shows that in addition

to ethylenedipyridyl bromide some bromoethylpyridyl bromide (*platinichloride*, $[C_5H_5NCl \cdot C_2H_4Br]_2, PtCl_4$, long needles, m. p. 220°) is formed. In isolating the substance, the mother liquors were treated with platinic chloride, and in this way the following double *platinichlorides* and *aurichlorides* with pyridine were obtained.

(1). $[C_5H_5N, HCl]_2, PtCl_4 + [C_5H_5NCl \cdot C_2H_4Cl]_2, PtCl_4$, reddish-yellow leaflets, m. p. 195°; $C_5H_5N, HAuCl_4 + C_5H_5NCl \cdot C_2H_4Cl, AuCl_3$, glancing needles, m. p. 142—143°.

(2). $[C_5H_5N, HCl]_2, PtCl_4 + C_5H_5NCl \cdot C_2H_4Cl, PtCl_4$, yellowish-brown, nodular crystals, m. p. 180—181°; the corresponding *aurichloride* formed leaflets, m. p. 155°.

Ethylenedipyridyl chloride, $C_2H_4[C_5H_5NCl]_2$, obtained by treating the bromide with silver chloride in water or by the direct action of ethylene chloride on pyridine, crystallises in leaflets or tablets, both forms containing alcohol of crystallisation, and does not melt at 260°. The *aurichloride*, $B, 2AuCl_3$, forms small, leafy crystals from dilute alcohol. The *picrate*, m. p. 246°, forms yellow leaflets. *Chloroethylpyridyl chloride* is a hygroscopic, syrupy mass; the *platinichloride*, m. p. 218° (decomp.), forms needles, and the *aurichloride*, m. p. 135—136°, needles or leaflets, from water.

[With A. SEEBERG.]—On heating bromoethylpyridyl bromide with silver nitrate in aqueous solution, pyridinecholine is produced. This yields an aurichloride, m. p. 117°, crystallising in broad needles or leaflets, a platinichloride, m. p. 179°, forming reddish-yellow tablets, and a *mercurichloride*, m. p. 188—189°, as a colourless, crystalline powder (compare Roithner, A., 1895, i, 319, and Litterscheid, A., 1902, i, 308).

When silver oxide is used the product is pyridineneurine, which yields an aurichloride, m. p. 178°, crystallising in long, yellow needles, and a platinichloride, m. p. 193° (decomp.), forming small tablets.

T. A. H.

Kynurenic Acid. (Miss) ANNIE HOMER (*Proc. Physiol. Soc.*, 1913, xviii; *J. Physiol.*, 46).—The kynurenic acid of dog's urine is 2-hydroxyquinoline-4-carboxylic acid. It has m. p. 288—289°; this is a higher figure than that given by previous workers. ' W. D. H.

The Ten Stereoisomeric Tetrahydroquinaldinomethylene-camphors. WILLIAM J. POPE and JOHN READ (*Proc. Camb. Phil. Soc.*, 1913, 17, [2], 204).—The two enantiomorphously related tetrahydroquinaldines condense readily with the two similarly related oxymethylenecamphors, yielding products of the constitution

$$C_{10}H_{12}N \cdot CH:C \Big\langle {}^{C_8H_{14}}_{CO}.$$
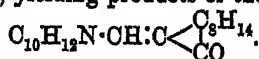
Since each component of the condensation can be obtained in a dextro- and a lævo-rotatory form, four simple optically active condensation products can be obtained, represented by the configurations: (1) *d-D*, (2) *l-L*, (3) *d-L*, (4) *l-D* (*d-* and *l-* represent the configurations of the tetrahydroquinaldine residue, and *D-* and *L-* those of the oxymethylenecamphor nucleus). From these the two racemic compounds (5) [*d-D*, *l-L*] and (6) [*d-L*, *l-D*] can be prepared, whilst in the present

instance the following two pairs of partly racemic compounds are also obtainable: (7) [*d-D*, *d-L*], (8) [*l-L*, *l D*], (9) [*d-D*, *l-D*], and (10) [*l-L*, *d-L*].

It would be anticipated that no resolution of externally compensated tetrahydroquinaldine into its optically active components would be possible with the aid of *d*- or *l*-oxymethylenecamphor. It is shown, however, that on treating externally compensated tetrahydroquinaldine with less than one-half an equivalent of *d*-oxymethylenecamphor, a resolution can be effected because the *l*-base condenses more rapidly than the *d*-isomeride with *d*-oxymethylenecamphor; under these conditions the condensation yields about 80% of the partly racemic compound (9) and 20% of the optically active substance (4), from which *l*-tetrahydroquinaldine may be separated. II. W.

Preparation of Hydroxycarbazole.

Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 258298. Compare A., 1907, i, 1074; T., 1911, 99, 103).—*Carbazoletrisulphonic acid* is obtained when carbazole (3 parts) dissolved in concentrated sulphuric acid (10 parts) is gently warmed with 3 parts of fuming sulphuric acid (20% SO_3).

Potassium carbazoletrisulphonate forms colourless crystals, and when fused with potassium hydroxide (3 parts), first at 190—200° and subsequently at 220—230°, furnishes the crystalline *potassium hydroxycarbazoledisulphonate*.

1-*Hydroxycarbazole* (annexed formula), colourless leaflets, m. p. 163°, is obtained when the foregoing potassium hydroxycarbazole disulphonate is heated with 5% sulphuric acid during five hours at 180°, and is not identical with the hydroxycarbazole (m. p. 255—256°) prepared by Ruff and Stein (A., 1901, i, 620).

F. M. G. M.

Action of Formic Acid on Triphenylmethane Dyes.

Alfred Guyot and A. Kovache (*Compt. rend.*, 1913, 156, 1324—1327. Compare A., 1912, i, 186, 972).—Hexamethyl-violet and malachite-green are only very slightly reduced by pure formic acid. The addition of sodium formate, however, causes rapid reduction with the evolution of carbon dioxide, which takes place in two stages, the second requiring the presence of a large amount of formate. The hexamethyl violet is first reduced like the simple triarylcarbinols (*loc. cit.*), and gives hexamethyltriaminotriphenylmethane, which then undergoes further reduction to dimethylaniline and tetramethyl-*p* diaminodiphenylmethane, with the evolution of a second molecule of carbon dioxide. This reduction is quantitative, whereas with malachite-green the reduction, whilst proceeding similarly, is never quantitative in the second stage. The authors consider that this action of formic acid establishes evident relationship and a complete continuity between the dyes proper and the carbinols deprived of all auxochrome; between these two groups there only exists a difference in reactional aptitude, which can be attributed to the more or less pronounced basicity of the molecules, and which shows itself in the varying ease with which reduction takes place from one member to another. W. G.

Tetrachlororhodamines. MARCEL BLOCH (*Bull. Soc. ind. Mul-house*, 1913, **83**, 81—84).—When an equimolecular mixture of *m*-dimethylaminophenol and tetrachlorophthalic anhydride is heated at 165°, *tetramethyltetrachlororhodamine phthalate* is obtained, which, by the successive action of sodium hydroxide and hydrochloric acid, is converted into the corresponding *hydrochloride*, green crystals, from which the free *base* is obtained by addition of sodium hydroxide. The latter dyes cotton, wool, and silk in reddish-violet shades exhibiting, in the case of the latter fibre, a magnificent fluorescence. The colours are stable towards light and alkalis. Attempts to esterify the rhodamine were unsuccessful, probably owing to the presence of electronegative atoms in the ortho-position to the carboxyl group.

When *m*-dimethylaminophenol is heated with tetrachlorophthalic anhydride in xylene solution, *o-4-dimethylamino-2-hydroxybenzoyltetra-chlorobenzoic acid*, $NMe_2 \cdot C_6H_3(OH) \cdot CO \cdot C_6Cl_4 \cdot CO_2H$, is formed together with a *substance*, separating from glacial acetic acid in yellow needles, which probably has the formula $C_6Cl_4(CO \cdot O \cdot C_6H_4 \cdot NMe_2)_2$.

By the condensation of tetrachlorophthalic anhydride with *m*- or *p*-phenylenediamine or their alkylated derivatives in glacial acetic acid solution, a series of yellow *compounds* has been prepared which yield colourless salts with hydrochloric acid. Results of analyses are in agreement with the general formula:

$$CO<^{C_6Cl_4}_{O}>C:N \cdot C_6H_4 \cdot NR_2.$$
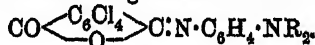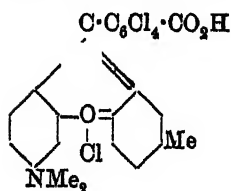
Tetrachloroaporhodamine (annexed formula) is formed by the condensation of 4-dimethyl-amino-2-hydroxy-*o*-benzoyltetrachlorobenzoic acid with *p*-cresol in the presence of concentrated sulphuric acid, whilst with resorcinol or pyrogallol the same acid yields substituted rhodols.

H. W.

[**Preparation of Hydroxyphenylhydrazinesulphonic Acids and their Condensation Products.**] FARBWERK MÜHLHEIM vorm. A. LEONHARDT & Co. (D.R.-P. 258017).—When the *o*-hydroxyphenyl-hydrazines are condensed with *o*-diketones they give rise to dyes, and the preparation of the following substituted hydrazines by diazotisation and reduction of the corresponding bases is described: *4-hydroxy m-tolylhydrazine-5-sulphonic acid* (I); *2-hydroxy-1-naphthylhydrazine-4-sulphonic acid* (II), and its *tolylsulphonyl* ester (III); *3-nitro-2-hydroxyphenylhydrazine-5-sulphonic acid* (IV), and *5-nitro-4-hydroxy-m-tolylhydrazine* (V), whilst the tinctorial properties of the *compounds* obtained by condensing them with camphorquinone, phenanthraquinone, and other *o*-diketones are tabulated in the original.

(IV.)   (V.)
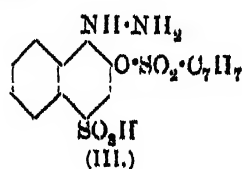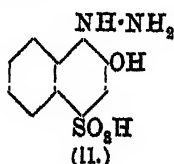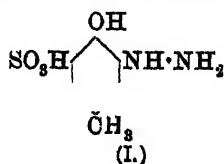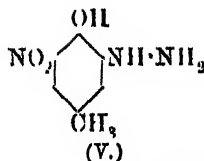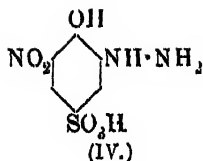
F. M. G. M.

Hydrazones of Hydroxy-aldehydes and -ketones; Alkali-insoluble Naphthols. HENRY A. TORREY and CARL M. BREWSTER (*J. Amer. Chem. Soc.*, 1913, **35**, 426—444).—Torrey and Kipper (A., 1907, i, 325 ; 1908, i, 460) have shown that the insolubility of certain phenols in aqueous alkali hydroxides depends (1) on the hydroxyl group being in the ortho-position to a large side-chain, and (2) on the other substituting groups in the benzene nucleus to which the hydroxyl group is attached. In the present paper an account is given of certain naphthol derivatives which are insoluble in alkali hydroxide solutions.

The naphthalene group, $\overset{C:C-}{\underset{C:C-}{|}}$, is more effective in producing insolubility than any other group yet studied. There does not seem to be any marked difference between the derivatives of 1-hydroxy-β-naphthyl methyl ketone (2-acetyl-1-naphthol) and naphthaldehyde; the phenyl-hydrazones, p-bromophenylhydrazones, phenylbenzylhydrazones, α- or β-naphthylhydrazones, and the benzidine compounds of both substances show the same insolubility.

The following compounds of 1-hydroxy-β-naphthyl methyl ketone are described. The *α-naphthylhydrazone*, $OH \cdot C_{10}H_6 \cdot CMe:N \cdot NH \cdot C_{10}H_7$, m. p. 179—180°, insoluble in boiling aqueous sodium hydroxide; the *β-naphthylhydrazone*, m. p. 174—176°, insoluble in warm 10% sodium hydroxide; the *phenylbenzylhydrazone*, m. p. 130—132°, insoluble in boiling 10% sodium hydroxide ; the *azine*, which decomposes at a high temperature and is insoluble in warm 10% sodium hydroxide, and its *acetate*, m. p. 169—170°; the *benzidine* compound,

$$C_{12}H_8(N:CMe \cdot C_{10}H_6 \cdot OH)_2,$$
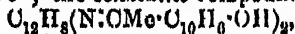
decomposing at 210°, and insoluble in boiling 10% and 30% sodium hydroxide ; the *semicarbazone*, m. p. 245—250°, easily soluble in cold aqueous sodium hydroxide ; the *β-naphthylimide*,

$$OH \cdot C_{10}H_6 \cdot CMe:N \cdot C_{10}H_7,$$
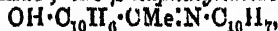
m. p. 161—162°, insoluble in boiling 10% sodium hydroxide ; and the p-*aminophenol* compound, $OH \cdot C_{10}H_6 \cdot CMe:N \cdot C_6H_4 \cdot OH$, which decomposes at 210—220° and is easily soluble in cold aqueous sodium hydroxide.

1 : 5-*Diphenyl-3-α-naphtholpyrazoline*, $OH \cdot C_{10}H_6 \cdot C_8H_3N_2Ph_2$, m. p. 189° (decomp.), prepared by the action of phenylhydrazine on 2-benzyl-ideneacetyl-1-naphthol (Kostanecki, A., 1898, i, 373), is insoluble in boiling 10% and 30% aqueous sodium hydroxide.

Bromo-1-hydroxy-β-naphthyl methyl ketone, $OH \cdot C_{10}H_5Br \cdot COMe$, has been described in an earlier paper (Torrey and Brewster, A., 1910, i, 48). The *acetyl* derivative, m. p. 95—96°, is insoluble in cold sodium hydroxide solution, but gradually decomposes on warming ; the

a-naphthylhydrazone, m. p. 175—176° (decomp.), is insoluble in boiling 10% sodium hydroxide; the *β-naphthylhydrazone*, m. p. 184 -186° (decomp.), and *phenylbenzylhydrazone*, m. p. 125—126°, are insoluble in warm 10% sodium hydroxide; the *oxime*, m. p. 189—190° (decomp.), yields with sodium hydroxide a green, slightly soluble salt; the *semicarbazone* and *azine* decompose at a high temperature; the former dissolves readily in dilute alkali hydroxide, whilst the latter is insoluble in boiling 10% sodium hydroxide.

The following compounds of 4-nitro-1-hydroxy-β-naphthyl methyl ketone are described. The *phenylhydrazone*, m. p. 222—223° (decomp.), imparts a red colour to cold 10% sodium hydroxide, and gradually dissolves on heating; it is insoluble in a 30% solution, however, and is decomposed when boiled with this reagent. The *a-naphthylhydrazone* decomposes at a high temperature, is insoluble in cold aqueous sodium hydroxide, but on warming renders the solution yellow. The *β-naphthylhydrazone* decomposes at 240°; it is insoluble in cold sodium hydroxide, but decomposes when heated with the solution. 4-*Nitro*-1-*acetoxy-β-naphthyl methyl ketone phenylhydrazone acetate*,

$$OAc \cdot C_{10}H_5(NO_2) \cdot OMe \colon N \cdot NAcPh,$$
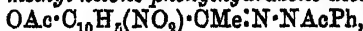
has m. p. 197—198°.

β-Hydroxynaphthaldehydephenylhydrazone is insoluble in cold aqueous sodium hydroxide, and decomposes slightly when the solution is heated. The p-*bromophenylhydrazone*, m. p. 194—195° (decomp.), the *phenylbenzylhydrazone*, m. p. 152—153°, and the benzidine *compound*, $C_{18}H_8(N \cdot CH \cdot C_{10}H_6 \cdot OH)_2$, are insoluble in boiling 10% sodium hydroxide. The *semicarbazone*, m. p. above 240° (decomp.), is readily soluble in cold 10% sodium hydroxide. The *phenylhydrazone* of the *acetyl* derivative, $OAc \cdot C_{10}H_6 \cdot CH \colon N \cdot NHPh$, m. p. 164—165°, slowly decomposes when heated with sodium hydroxide solution. The *azine acetate*, $OAc \cdot C_{10}H_6 \cdot CH \colon N_2 \colon CH \cdot C_{10}H_6 \cdot OH$, has m. p. 183—185°. β-Hydroxynaphthaldehyde yields two oximes, one of m. p. 148--150° (Horlacher, *Diss.*, 1899), and the other, m. p. 158—160°.

Bromo-1-*hydroxy-β-naphthyl dibromophenylethyl ketone* (*benzylidene*-2-*acetyl* 1-*naphthol tribromide*), $OH \cdot C_{10}H_5Br \cdot CO \cdot CHBr \cdot CHPhBr$, m. p. 199°, is slightly soluble in boiling 10% sodium hydroxide, but insoluble in a boiling 30% solution.

4-*Bromo*-1-*hydroxynaphthyl furfurylidenemethyl ketone*,

$$OH \cdot C_{10}H_5Br \cdot CO \cdot CH \colon CH \cdot C_4H_4O,$$
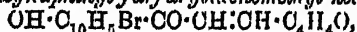
m. p. 154—155°, and the corresponding *piperonylidene* compound, decomposing at 209—214°, are insoluble in boiling 30% sodium hydroxide. The p-*nitrobenzylidene* compound, m. p. 194—195°, is slightly soluble in 10% sodium hydroxide, but insoluble in a 30% solution.

o-Hydroxyacetophenonephenylhydrazone is readily soluble in dilute sodium hydroxide. o-*Acetoxybenzaldehydephenylbenzylhydrazone* has m. p. 137—139°. Benzidine bis-salicylaldehyde is insoluble in cold 10% sodium hydroxide, whilst the corresponding azine is readily soluble. 5-*Bromo*-2-*acetoxybenzaldehydeacetylphenylhydrazone*,

$$OAc \cdot C_6H_3Br \cdot CH \cdot N \colon NAcPh,$$

has m. p. 135—136°. 5-*Bromosalicylaldehydeazine*, m. p. 305—307° (decomp.), is readily soluble in cold 10% sodium hydroxide.   E. G.

The Optically Active Semicarbazone and Benzoylphenyl-hydrazone of *cyclo*Hexanone-4-carboxylic Acid. WILLIAM H. MILLS and (Miss) ALICE M. BAIN (*Proc. Camb. Phil. Soc.*, 1913, **17**, 203).—The *semicarbazone* of *cyclo*hexanone 4-carboxylic acid can be obtained in an optically active form by crystallising its *morphine* salt from dilute alcohol, the highest value obtained for the molecular rotation in alkaline solution being $[M]_D + 38·8°$. The *benzoylphenyl-hydrazone* of the acid can similarly be obtained in an optically active form by crystallisation of its *quinine* salt from aqueous alcohol, the highest value found for the molecular rotation in alkaline solution being $[M]_D + 238·6°$.

These optically active compounds agree so closely in their behaviour with the optically active oxime of this acid previously described by the authors (T., 1910, **97**, 1866) that there can be little doubt that the optical activity is due to similar causes in the three cases. The observations, accordingly, lend great support to the view that stereoisomerism in the sense of the Hantzsch-Werner hypothesis exists in the case of semicarbazones and phenylhydrazones.   H. W.

Synthesis of Hydroxypyrrole and Pyrroline Derivatives from Ethyl Aminocrotonate. ERICH BENARY and BOLESLAV SILBERMANN (*Ber.*, 1913, **46**, 1363—1375).—As might be expected, ethyl β-amino-α-chloroacetylcrotonate (A., 1909, i, 888) readily yields pyrrole derivatives when deprived of the elements of hydrogen chloride. The product $NH{<}^{CMe:C·CO_2Et}_{CH=C·OH}$ (I.) gives a coloration with ferric chloride which is considered to be characteristic of a hydroxy-pyrrole, but in some cases it reacts in the tautomeric ketonic form $NH{<}^{CMe:C·CO_2Et}_{CH_2-CO}$ (II.), and yields, *e.g.*, a dipyrroline derivative, $CO_2Et·C{<}^{CO}_{CMe·NH}{>}C:C{<}^{CO}_{NH·CMe}{>}C·CO_2Et$ (III.), on oxidation and an indoxylpyrroline, $CO_2Et·C{<}^{CO}_{CMe·NH}{>}C:C{<}^{CO}_{NH}{>}C_6H_4(IV.)$, on condensation with isatin.

The ester (I.) could not be hydrolysed, but it condenses in cold concentrated hydrochloric acid to form two bi-molecular compounds which can be easily transformed into one another, and to which the formulæ $CO_2Et·C{<}^{C(OH)}_{CMe·NH}{>}C·C{<}^{C(CO_2Et)·}_{CH·NH--}{>}CMe$ (V.) and $CO_2Et·C{<}^{C(OH)_2}_{CMe·NH}{>}C:C{<}^{C(CO_2Et)·}_{CH_2·NH--}{>}CMe$ (VI.) are assigned.

Like other pyrrole derivatives with a free α-position, the ester couples with phenyldiazonium chloride and forms the compound $CO_2Et·C{<}^{C(OH)}_{CMe·NH}{>}C·N:NPh$ (VII).

With nitrous acid it yields the oximino-compound, $CO_2Et·C{<}^{CO}_{CMe·NH}{>}C:N·OH$ (VIII.),

which exists in two forms, but with sodium nitrite and glacial acetic acid it gives a nitroimine, $CO_2Et\cdot C\underset{CMe\cdot NH}{\overset{CO}{<}}>C\!:\!N\cdot NO_2$ (IX.) (compare Scholl, A., 1905, i, 181; 1906, i, 767), which behaves in water as a nitroiminic acid, analogous to nitroic acid (Hantzsch and Kissel, A., 1900, i, 89). The acidity is not due to the hydrogen atom of the imino-group, since this may be replaced by methyl without affecting that property.

The methylated nitroimine (X.) is slowly hydrolysed by cold alkali, when the nitroamide of acetoneoxalic acid (XI.) is formed with elimination of methylamine, alcohol, and carbon dioxide :

$$CO_2Et\cdot C\underset{CMe\cdot NMe}{\overset{CO}{<}}>C\!:\!N\cdot NO_2 \text{ (X.)} \longrightarrow$$

$$CH_3\cdot CO\cdot CH_2\cdot CO\cdot CO\cdot NH\cdot NO_2 \text{ (XI.).}$$
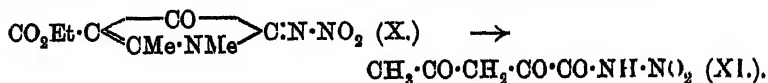
Ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate (I.) is prepared by the addition of ethyl β-amino-α-chloroacetylcrotonate to alcoholic potassium hydroxide. It forms faintly yellow leaflets which decompose at 215°, reduces ammoniacal silver oxide, gives the pyrrole reaction, and produces a brown coloration in alcohol or a red precipitate in water with ferric chloride. It gives a dark red solution in cold concentrated hydrochloric acid which becomes green in time, and contains a mixture which on fractionation from alcohol deposits the *hydrate* of *ethyl 3-keto-5 : 5'-dimethyl-2 : 3'-dipyrroline-4 : 4'-dicarboxylate* (VI.) in reddish-brown needles, which are purified by conversion into the unstable, greenish additive compound with hydrochloric acid and leaving in vacuum. It gives no coloration with ferric chloride, and decomposes at 180°. The alcohol mother liquors contain *ethyl 3-hydroxy-5 : 5'-dimethyl-2 : 3'-dipyrrole-4 : 4'-dicarboxylate* (I.), which is precipitated by water, or obtained from the foregoing compound by the action of water, in the form of almost colourless leaflets which decompose at 157·5°, and give the above compound with hydrochloric acid and a transient green colour with ferric chloride. The indigoid *ethyl bis-2-methylpyrroline-3-carboxylate* (III.) is obtained in brick-red, microscopic needles, decomp. 220— 225°, which give a dark red potassium salt with alcoholic potassium hydroxide. The leuco-compound is grey, but is rapidly oxidised in the air. The *ethyl 2-indoxylpyrrolinecarboxylate* (IV.) is a dark red powder, decomp. 220—225°. *Ethyl 5-benzeneazo-4-hydroxy-2-methylpyrrole-3-carboxylate* (VII.) forms brownish-yellow needles, decomp. 225—226°, which give a red colour with ferric chloride in alcohol.

On treating the ester (I.) with sodium nitrite and dilute hydrochloric acid, the α-form of *ethyl 5-oximino-4-keto-2-methylpyrroline 3-carboxylate* (VIII.) is obtained. It is purified by means of its potassium salt, and then forms light yellow needles, decomp. 175°. When a few drops of hydrochloric acid are added to the warm alcoholic solution, the β-form crystallises in olive-green leaflets. *Ethyl 5-nitroimino-4-keto-2-methylpyrroline-3-carboxylate* (IX.) forms shining yellow, flat needles with $1H_2O$, which dissolve in dilute alkalis, give precipitates with silver and lead salts, and respond to the Liebermann and Thiele-Lachman reactions. Both the hydrate

and the anhydrous compound give a brown *additive* compound, $C_8H_9O_5N_3.NH_3$, with ammonia.

Ethyl β-methylamino-α-chloroacetylcrotonate,

$$NHMe \cdot CMe \vdots C(CO \cdot CH_2Cl) \cdot CO_2Et,$$

from ethyl methylaminocrotonate and chloroacetyl chloride in presence of pyridine in ether, forms long, white needles, m. p. 50·5—51°. With alkali it yields *ethyl 4-hydroxy-1 : 2-dimethylpyrrole-3-carboxylate* as a very hygroscopic mass, which, with nitrous acid, gives the analogous iso*nitroso*-compound, $C_9H_{12}O_4N_2$, in lemon-yellow needles, decomp. 162·5°, which are hydrolysed by cold sodium hydroxide to the *acid*, $C_7H_8O_4N_2$, colourless needles, decomp. 154—155°. The *nitroimino*-compound (X.) is formed by the action of sodium nitrite and glacial acetic acid in orange needles with $1H_2O$, decomp. 200°, which give a brown *additive* compound with ammonia, and dissolve in sodium carbonate solution. The addition of dilute hydrochloric acid after eighteen hours to the red solution in sodium hydroxide precipitates *acetylpyruvonitroamide* (XI.) in colourless needles, decomp. 258°, which reduce ammoniacal silver oxide, and give a red coloration with ferric chloride. With phenylhydrazine it forms an indole *compound*, $C_{17}H_{16}O_2N_5$, in brick-red, soft needles, decomp. 244°, ammonia being eliminated.　　　　J. C. W.

Syntheses in the Group of the Indogenides. ANDRÉ WAHL and P. BAGARD (*Compt. rend.*, 1913, **156**, 1382—1385).—Condensation of oxindole with cyclic aldehydes and isatin or its chloride in acetic acid solution yields, respectively, *iso*indogenides, *iso*indigotin, and indirubin (compare A., 1909, i, 330, 735). This reaction has now been extended, firstly by modifying the conditions of the reaction, and secondly by using substituted isatins.

Oxindole and isatins condense in alcoholic solution under the influence of sodium ethoxide, giving colourless products, constitutions of which have not yet been determined.

In concentrated sulphuric acid the condensation is accompanied by sulphonation, yielding *iso*indigotindisulphonic acid, which is isolated in the form of its *sodium* salt, $C_{16}H_8N_2O_2(SO_3Na)_2,2H_2O$, crystallising in brown leaflets, which become anhydrous at 100°. It is an acid colour, dyeing wool reddish-orange. Other salts have been prepared, namely : the *calcium* salt, red needles, crystallising with $5H_2O$; the *barium* salt, an amorphous, red powder; the *silver* salt, red needles, crystallising with $2H_2O$; the *nickel* salt, reddish-brown crystals, containing $5H_2O$. By decomposing the barium salt with the calculated quantity of sulphuric acid, the free *acid*, "*iso*indigo-carmine," is obtained, which is very soluble in alcohol and water, and yields an equally soluble *ammonium* salt on the addition of ammonia.

If oxindole is condensed with substituted derivatives of isatin in acetic acid solution, unsymmetrically-substituted derivatives of *iso*-indigotin are obtained, thus :

$$C_6H_4 \begin{array}{c} CH_2 \\ NH \end{array} \hspace{-2mm} > \hspace{-2mm} CO + CO \begin{array}{c} CO \\ NH \end{array} \hspace{-2mm} > \hspace{-2mm} C_6H_3X =$$

$$H_2O + NH \begin{array}{c} C_6H_4 \\ CO \end{array} \hspace{-2mm} > \hspace{-2mm} C:C \begin{array}{c} C_6H_3X \\ CO \end{array} \hspace{-2mm} > \hspace{-2mm} NH.$$
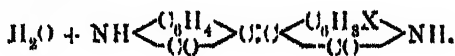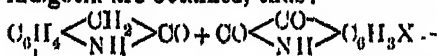
By this means *brom*oiso*indigotin*, *dibrom*oiso*indigotin*, *methyl*iso-*indigotin*, and *nitro*iso*indigotin*, all crystalline compounds, have been prepared.

By the interaction of substituted isatin chlorides and oxindole in benzene solution, substituted indirubins of the type

$$NH{<}^{C_6H_4}_{CO}{>}C{:}C{<}^{CO}_{NH}{>}C_6H_3X$$
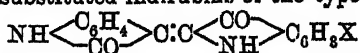
are obtained, isomeric with those prepared by Baeyer's condensation with indoxyl and isatins (compare A., 1911. i, 164, 577). These new indirubins, thus obtained, have a violet colour and dissolve in sodium hyposulphite, giving yellow dye liquors. The mono-substituted derivatives are only slightly fixed on the fibre. Nitroindirubin dyes a violet-black, due to the reduction of the nitro-group by the hyposulphite.

<div align="right">W. G.</div>

The Condensation of *para*Quinones with Reduced Heterocyclic Nitrogen Compounds. JULIUS SCHMIDT and AUGUST SIGWART (*Ber.*, 1913, 46, 1491—1497. Compare Möhlau and Redlich, A., 1912, 1, 129).—The observation that hexahydrocarbazole when mixed with *p*-benzoquinone in alcoholic solution yields a violet-red liquid from which brown crystals, m. p. 199—200°, soon separate (A., 1912, i, 616) has now been followed up. The product has the composition $C_6H_2O_2(C_{12}H_{14}N)_2$, that is, bishexahydrocarbazyl-*p*-benzoquinone, analogous to the dianilino-*p*-benzoquinones (Zincke, A., 1883, 1117) and to diethyldiamilino-*p*-benzoquinone (Fischer and Schrader, A., 1910, i, 270). Carbazole and dihydro- and tetrahydro-carbazole do not form such compounds, probably on account of their feebler basic character.

Piperidine and *p*-benzoquinone mixed in cold alcoholic solution give a brownish-violet coloration, followed by a deposit of brownish-violet needles with a steel-blue lustre, m. p. 172°; the substance is *dipiperidyl*-p-*benzoquinone*, $C_5NH_{10}{\cdot}C{<}^{CH\cdot CO}_{CO\cdot CH}{>}C{\cdot}C_5NH_{10}.$

The condensation product of *p*-benzoquinone with tetrahydroquinoline has already been described (Möhlau and Redlich, *loc. cit.*); 1-methyltetrahydroquinoline and 9-methylhexahydrocarbazole gave no condensation products, the crystalline deposit obtained in each case consisting of quinol. Pyrrole reacted with *p*-benzoquinone in alcoholic solution, but the dark crystalline powder, m. p. above 360°, was abnormal in composition, equimolecular quantities of the two substances apparently having entered into reaction. Coniine gave a deep coloration, but no solid product. Pyridine, quinoline, and *iso*quinoline caused only depositions of a nitrogen-free solid, which probably is some polymerisation product of quinone or quinhydrone.

Toluquinone gives rise to condensation products of small crystallising power, for although the expected colorations were obtained with piperidine and hexahydrocarbazole, no crystalline deposits could be obtained; tetrahydroquinoline gives a crystalline compound with toluquinone, but this has already been described (Möhlau and Redlich, *loc. cit.*). Naphthaquinone with hexahydrocarbazole, piperidine, and

tetrahydroquinoline gave deep red alcoholic solutions, but the deposit in each case consisted merely of naphthaquinhydrone.

Tetrachloro-p-benzoquinone (chloranil) behaves like p-benzoquinone with piperidine, producing *dipiperidyldichloro-p benzoquinone*,

$$C_5NH_{10}\cdot C\!\!<^{CCl\cdot CO}_{CO\cdot CCl}\!\!>C\cdot C_5NH_{10},$$
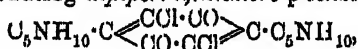
lustrous, bluish-black needles, m. p. 143—144°.　　　　　D. F. T.

Action of isoQuinoline on 1 : 3-Dichloro-4 : 6-dinitrobenzene.

THEODOR ZINCKE and G. WEISSPFENNING (*Annalen*, 1913, **397**, 255—273).—isoQuinoline and 1 : 3-dichloro-4 : 6 dinitrobenzene react in warm ether to form, after fourteen to fifteen days, *dinitrophenyldi-isoquinolinium dichloride*, $C_9H_7NCl\cdot C\!\!<^{C(NO_2)=\!=\!=CH}_{CH\cdot C(C_9H_7NCl)}\!\!>C\cdot NO_2$, and an orange-red, crystalline ψ-*base*, $C_{15}H_{10}O_5N_3Cl$, m. p. 168° (decomp.), blackening at about 100°.

In its behaviour, dinitrophenyldiisoquinolinium dichloride resembles partly dinitrophenyldipyridinium dichloride (A., 1910, i, 585), partly 2-op dinitrophenylisoquinolinium chloride (this vol , i, 389). From it an orange-yellow *dichromate*, yellow *picrate*, m. p. 225°, and *platini-chloride*, m. p. 250°, can be prepared. By treating its aqueous solution with sodium carbonate or ammonia, a ψ-*base* is obtained, a brownish-red powder, which is regarded as a dicarbinol base,

$$^{C_6H_4\cdot OH(OH)}_{OH=\!=\!=CH}\!\!>N\cdot C_6H_2(NO_2)_2\cdot N\!\!<^{CH(OH)\cdot C_6H_4}_{OH=\!=\!=CH}.$$
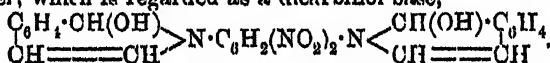
This ψ-base regenerates salts of dinitrophenyldiisoquinolinium by treatment with acids, is converted into the yellow betaine (see below) by boiling dilute acetic acid, reacts with warm alcohols to form

carbinyl ethers, $^{C_6H_4\cdot CH(OR)}_{CH=\!=\!=CH}\!\!>N\cdot C_6H_2(NO_2)_2\cdot N\!\!<^{CH(OR)\cdot C_6H_4}_{CH=\!=\!=CH}$

(*methyl ether*, decomp. 180 --190°, long, red needles; *ethyl ether*, m p. 172°, red needles), and forms a *dihydrazide*,

$$C_6H_2(NO_2)_2(NH\cdot CH\!:\!CH\cdot C_6H_4\cdot CH\!:\!N\cdot NHPh)_2,$$
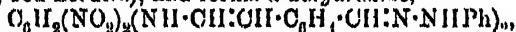
almost black crystals, by warming with alcoholic phenylhydrazine. In methyl alcoholic solution the ψ base is converted by nitric acid, D 1·4, into the very characteristic *dinitrophenyldiisoquinolinium dinitrate*, $C_6H_2(NO_2)_2(C_9H_7N\cdot NO_3)_2,H_2O$, decomp. 140—150°, colourless needles.

By long keeping with 10% sodium nitrite, dinitrophenyldiisoquinolinium dichloride is converted into the *betaine*,

$$C_6H_2(NO_2)_2\!\!<^{O}_{C_9NH_7},$$
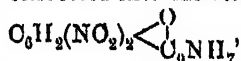
yellow needles. The constitution of the latter, which is also obtained by treating the ψ-base with boiling 25—30% acetic acid, is proved by the formation of the substance from isoquinoline and 3-chloro-4 : 6-dinitrophenol at 100°. The betaine forms salts (*chloride*, colourless needles, *platinichloride*, *nitrate*) which are hydrolysed by an excess of water. A corresponding *thiobetaine*, $C_6H_2(NO_2)_2\!\!<^{S}_{C_9NH_7}$, dark

crimson powder, is obtained by treating alcoholic dinitrophenyldiisoquinolinium dinitrate with hydrogen sulphide; it forms a very unstable *chloride* and *platinichloride*.

The ψ-base, $C_{15}H_{10}O_5N_3Cl$, behaves similarly to the ψ-base obtained from 2-*op*-dinitrophenyl*iso*quinolinium chloride (*loc. cit.*), and proves to be a chloro-derivative thereof. It has the constitution

$$\begin{matrix} C_6H_4 \cdot CH(OH) \\ CH === CH \end{matrix} > N \cdot C_6H_2Cl(NO_2)_2,$$
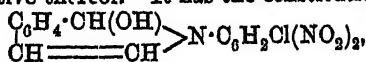
forms a *chloride*, $\begin{matrix} C_6H_4 \cdot CH \\ CH == CH \end{matrix} > NCl \cdot C_6H_2Cl(NO_2)_2$, colourless needles,

platinichloride, and *nitrate*, and yields ethers by treatment with alcohols in chloroform; the *methyl ether*, m. p. 164—165° (decomp.), dark red needles, and *ethyl ether*, m. p. 156—157°, red leaflets, are described. By boiling with alcohol and aniline, the ψ-base is converted into 2 - phenyl*iso*quinolinium chloride and 3 - chloro - 4 : 6 - dinitroaniline, the latter being changed to 2 : 4-dinitro-5-aminodiphenylamine by the excess of aniline.

By warming with water, the ψ-base is transformed into an *isomeride*, $C_{15}H_{10}O_5N_3Cl$, m. p. 168° (decomp.), dark violet-red leaflets, which forms salts with acids very slowly, and does not yield ethers or a hydrazide. On the contrary the ψ-base is converted by boiling alcoholic phenylhydrazine into the *hydrazide*,

$$NHPh \cdot N{:}CH \cdot C_6H_4 \cdot CH{:}OH \cdot NH \cdot C_6H_2Cl(NO_2)_2,$$
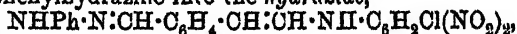
m. p. 155° (decomp.), blackish-red needles.　　　　　　　　　　　O. S.

Preparation of 5 : 5-Dialkylbarbituric Acids Containing an Unsaturated Hydrocarbon Residue Attached to Nitrogen. EMANUEL MERCK (D.R.-P. 258058. Compare A., 1899, i, 16 ; 1904, i, 380).—5 : 5-*Diethyl-1-allylbarbituric acid*, m. p. 77°, is obtained by heating monoallylcarbamide (20 parts) with diethylmalonyl chloride (40 parts) during fifty hours at 100—120°, whilst the latter compound with diallylcarbamide (sinapoline) furnishes 5 : 5-*diethyl-1 : 3-diallyl barbituric* acid, b. p. 153—157°/9 mm.　　　　　　F. M. G. M.

Pyrimidines. LXII. Syntheses of Pyrimidines Related Structurally to Pyrimidine-Nucleosides. TREAT B. JOHNSON and LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1913, 35, 585 597 ; *J. Biol. Chem.*, 1913, 14, 307—320).—This work was undertaken with the object of establishing the constitution of the nucleosides. The simplest nucleoside of thymine, namely, 4-hydroxymethyl-5-methyl tetrahydropyrimid-2 : 6-dione, has been synthesised in the following manner.

When thiocarbamide is condensed with ethyl γ-ethoxy-α-methylacetoacetate (Johnson, this vol., i, 588) in presence of sodium ethoxide, 2-*thio-4-ethoxymethyl-5-methyltetrahydropyrimid-2 : 6-dione*,

$$NH < \begin{matrix} CS - NH \\ CO \cdot CMe \end{matrix} > C \cdot CH_2 \cdot OEt,$$
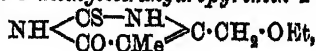
m. p. 191—192°, is obtained, which crystallises in hexagonal tablets. On boiling this substance with chloroacetic acid and water, it is converted into 4-*ethoxymethyl-5-methyltetrahydropyrimid-2 : 6-dione*,

$$NH < \begin{matrix} CO - NH \\ CO \cdot CMe \end{matrix} > C \cdot CH_2 \cdot OEt,$$

m. p. 220°, which forms arborescent crystals, and when heated with concentrated hydrochloric acid at 125—130° in a sealed tube yields 4-*chloromethyl-5-methyltetrahydropyrimid-2*: 6-*dione*,

$$NH<^{CO-NH}_{CO \cdot CMe}>C \cdot CH_2Cl,$$
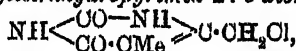
m. p. 243°, which crystallises in plates. By the action of silver acetate on this chloro-compound, the *acetyl* derivative,

$$NH<^{CO-NH}_{CO \cdot CMe}>C \cdot CH_2 \cdot OAc,$$
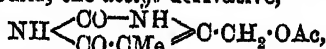
m. p. 260 —261° (decomp.), is produced, which is hydrolysed by barium hydroxide with formation of 4-*hydroxymethyl-5-methyltetrahydro-pyrimid-2*: 6-*di-one*, $NH<^{CO-NH}_{CO \cdot CMe}>C \cdot CH_2 \cdot OH$, m. p. 224—225° (decomp.), which crystallises in needles. An attempt to convert this simple nucleoside into thymine and formaldehyde by hydrolysis with 10% sulphuric acid was not successful, but on heating it with hydriodic acid and amorphous phosphorus it was converted into 4:5-dimethyl-tetrahydropyrimid-2: 6-dione (4:5-dimethyluracil). E. G.

Abnormal Solubility of Colloidal Uric Acid. LEOPOLD LIGHTWITZ (*Zeitsch. physiol. Chem.*, 1913, **84**, 416—418).—Polemical. Schade and Boden (this vol., i, 404) have regarded a supersaturated uric acid solution as a colloid gel. Their views are now criticised. The passage from the aggregate of molecules in drops to the amorphous solid phase, and from this to the crystalline form, takes place with very varying velocity, and the amorphous form can remain stable for a considerable time; it is therefore unnecessary to regard it as a colloid. E. F. A.

Purines. IX. 6:8 Dihydroxy-2-thiopurine and 6-Hydroxy-2:8-dithiopurine. The Desulphurisation of Thiopurines. A New Method of Preparing Xanthine. CARL O. JOHNS and ALBERT G. HOGAN (*J. Biol. Chem.*, 1913, **14**, 299—306).—6:8-*Di-hydroxy-2-thiopurine* is easily prepared in quantity by heating a mixture of 4:5-diamino-6-hydroxy-2-thiopyrimidine with carbamide.

6-*Hydroxy-2*:8-*dithiopurine* is obtained by heating a mixture of 4:5-diamino-6 hydroxy-2-thiopyrimidine and thiocarbamide.

Hypoxanthine-2-thiolacetic acid and 6:8-dihydroxypurine-2-thiolacetic acid can be boiled with water for hours without undergoing notable decomposition. When boiled with 20% hydrochloric acid they are hydrolysed to xanthine and uric acid respectively. 6-Hydroxypurine-2:8-dithiolacetic acid is more stable, and it is not desulphurised by boiling for several hours with 20% hydrochloric acid, although a small quantity of a dihydroxypurine monothiolacetic acid is obtained.

6:8-*Dihydroxy-2-thiopurine*, $^{NH-CO \cdot C \cdot NH}_{CS \cdot NH \cdot C \cdot NH}>CO$, forms minute needles, which do not melt at 310°; they give a brilliant murexide reaction. The corresponding 6:8-*dihydroxypurine-2-thiolacetic acid* has decomp. 225°.

Hypoxanthine-2-thiolacetic acid, $^{NH \cdot CO \cdot C \cdot NH}_{CO_2H \cdot CH_2 \cdot S \cdot C=N-C-N}>CH,$
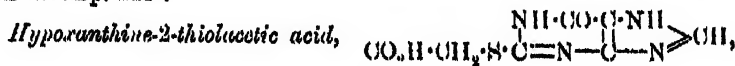
prepared by the action of monochloroacetic acid on thiohypoxanthine, decomposes at 240°, forming a violet-coloured substance. It is decomposed quantitatively on boiling with 20% hydrochloric acid into xanthine. This forms the most convenient procedure of preparing pure xanthine in quantity; it is not necessary to isolate the intermediate thiolacetic acid.   E. F. A.

Considerations and Experiments on the Constitution of the Azoxy-compounds. I. and II. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 201—213, 282—293).—A summary and discussion of the work of the author with various collaborators published in recent years.   R. V. S.

Polyazoxy-compounds. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 356—360).—The paper deals with the action of hydrogen peroxide in acetic acid solution on bisbenzeneazobenzene (Mills, T., 1895, **67**, 929) and on the new *compound*,

$$NPh{:}N{\cdot}C_6H_4{\cdot}NO{:}N{\cdot}C_6H_4{\cdot}N{:}NPh.$$
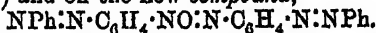
This substance is prepared by the action of sodium ethoxide on *p*-nitro-azobenzene ; it crystallises in red laminæ, m. p. about 215°.

Bisbenzeneazobenzene, when treated with hydrogen peroxide and glacial acetic acid, yields *bisbenzeneazoxybenzene*, $C_6H_4(N_2O{\cdot}Ph)_2$, which forms lustrous, yellow laminæ, m. p. 155°. It yields a *dibromo*-derivative, $C_{18}H_{12}O_2N_4Br_2$, which forms yellow crystals, m. p. about 200°. The azoxy-compound has, therefore, probably the formula

$$Ph{\cdot}NO{:}N{\cdot}C_6H_4{\cdot}NO{:}NPh.$$
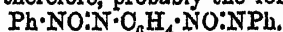
On treatment with concentrated sulphuric acid for one hour on the water-bath, it yields a product from which a substance, $C_{15}H_{14}ON_4$, can be extracted with benzene ; it forms yellowish-green leaflets, m. p. 185° (yielding a red liquid), and is probably the p-*hydroxyazo*-compound, $Ph{\cdot}N_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH.$

Azoxybisazoxybenzene, $Ph{\cdot}N_2O{\cdot}C_6H_4{\cdot}N_2O{\cdot}C_6H_4{\cdot}N_2O{\cdot}Ph$, is obtained from the corresponding triazo-derivative above mentioned; it forms lustrous, golden-yellow crystals, m. p. 230°. It yields a *dibromide*,

$$C_{24}H_{16}O_3N_6Br_2,$$
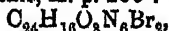
which is a yellow, microcrystalline powder, decomposing about 265°, and in consequence the structural formula of the azoxy-compound is probably $Ph{\cdot}N{:}NO{\cdot}C_6H_4{\cdot}NO{:}N{\cdot}C_6H_4{\cdot}NO{:}N{\cdot}Ph.$ The triazoxy-compound also suffers Wallach's re-arrangement, for on warming with sulphuric acid an intense blue coloration is obtained.   R. V. S.

The Relation between the Metallic Salts and the Soluble Carbonates and its Bearing on the Precipitation of Protein. W. NEVILL HEARD (*J. Physiol.*, 1913, **46**, 104—129).—Since thorough dialysis removes all precipitation of emulsoid protein by salts of the heavy metals, precipitation must be associated with some removable constituent. The experiment of adding salts to such dialysed solutions shows that the production of a substance with a very low solubility product is the necessary condition in causing precipitation. The only salt in the dialysate which is capable of producing this result is a hydrogen carbonate, except in the case of silver. The reaction of the metals with emulsoid protein closely follows the reaction of these

metals with soluble hydrogen carbonates, and the conclusion is therefore drawn that the process depends on this reaction. Probably the precipitation with hydrogen carbonates and carbonates acts mainly by the removal of the hydroxyl ions freed by the hydrolysis of these salts. But the results with silver nitrate and sodium chloride suggest that there are other factors.   W. D. H.

The Soluble Metallic Compounds of Sulphurised Proteins, with Special Reference to Copper. ROBERT UHL (*Zeitsch. physiol. Chem.*, 1913, 84, 478—496).—The preparation is described of sulphur-protein compounds from various proteins by means of carbon disulphide. It is analogous to the preparation of dithiocarbamates from aliphatic amines. These substances are converted by salts of the heavy metals in presence of alkali into metal-sulphur-protein compounds which are soluble in water, and in which the sulphur is united to the metal. The compounds with copper, silver, and mercury have a high content of metal, are resistant to alkali, are not precipitated by protein solutions, are resistant to proteolytic enzymes, and do not diffuse through an animal membrane. Sulphur-peptone given subcutaneously or intravenously is relatively non-toxic. Its copper compound is also relatively non-poisonous, and produces no local reaction; the animal resists doses of copper five times greater than when given in any other way. It is deposited in most of the organs except the brain and heart; most appears in the liver, and is then secreted into the bile. It has but little effect on blood pressure, and inhibits diuresis. It is bactericidal to staphylococci, but has no action on anthrax or trypanosomes.
                                                         W. D. H.

Method of Preparing Ash-free Caseinogen and Casein LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, 14, 203—206).—The ash-free proteins were prepared by alternate precipitation with dilute acid and solution in dilute ammonia several times, the last portion of calcium being removed by ammonium oxalate; after this the protein is precipitated with dilute acid and purified by treatment with water, alcohol and ether, being finally dried over sulphuric acid under reduced pressure. Elementary analyses are given of both proteins; the figures are very similar.   W. D. H.

Preparation and Composition of Basic Calcium Caseinogenate and Caseinate. LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, 14, 207--209).—Basic calcium caseinogenate and caseinate were prepared by treating the ash-free protein with calcium carbonate, or by dissolving the protein in lime-water and neutralising with hydrochloric acid. In the first reaction, the amount of carbon dioxide displaced by the protein was estimated, and also the amount of calcium in the resulting product. In the second method the calcium was also estimated. The compound contains 1·78% of calcium.
                                                         W. D. H.

Preparation and Composition of Unsaturated or Acid Caseinogenates and Caseinates. LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, 14, 211—225).—These were prepared

by dissolving the ash-free protein in $N/50$-sodium, potassium or ammonium hydroxide, and careful neutralisation with hydrochloric acid. The caseinates contain twice the amount of the basic element present in the caseinogenates. Such compounds are monobasic. With calcium, strontium, and barium, monobasic and dibasic compounds were obtained; in the caseinates twice the amount of base combines with the protein molecule as combines in the caseinogenates.   W. D. H.

Valency of Molecules, and Molecular Weights of Caseinogen and Casein. LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, 14, 227—230).—From the study of the caseinogenates and caseinates, the molecular weight of caseinogen is given as 8888, and of casein as 4444. The valency of the protein molecule in basic caseinogenates is 8, in basic caseinates, 4.   W. D. H.

Composition and Properties of the Brine-soluble Compound in Cheese. LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, 14, 231—236).—The protein in cheese which dissolves in warm 5% solution of sodium chloride is mono-calcium caseinate, formed from calcium caseinate by removal of part of its calcium by lactic acid produced from lactose in the process of cheese-making.   W. D. H.

Formation of Porphyrin. II. Porphyrinogen and its Relation to the Blood Pigment and its Derivatives. HANS FISCHER, ERICH BARTHOLOMÄUS, and HEINRICH ROSE (*Zeitsch. physiol. Chem.*, 1913, 84, 262—287. Compare this vol., i, 409).—Porphyrinogen, the first crystalline, colourless reduction product of the blood pigment, is obtained by the action at the ordinary temperature of glacial acetic acid and hydrogen iodide, in presence of phosphonium iodide, on hæmin, mesoporphyrin or hæmatoporphyrin. It is also obtained from the last two substances by reducing in alkaline solution with sodium amalgam, or with zinc dust and iron. Porphyrinogen is readily reconverted into mesoporphyrin by means of sodium methoxide, methyl alcoholic potassium hydroxide, alkaline potassium ferricyanide, or by exposure to atmospheric oxidation in neutral or alkaline solution.

Sodium methoxide splits off phyllopyrrole from porphyrinogen. The complete reduction is similar to that of hæmin. On oxidation, methyl ethylmaleinimide and hæmatic acid are obtained. When administered to animals, porphyrinogen has a sensibilising action, whereas mesoporphyrin has no action.

Use is made of the sparingly soluble sodium salt for the purification of mesoporphyrin. On total reduction of mesoporphyrin, phyllopyrrole is obtained with other products.   E. F. A.

Behaviour of the True Nucleic Acids to Dyes. II. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1913, 84, 309—328. Compare A., 1912, i, 926).—Nucleic acid gives precipitates with basic dyes, but none with acid dyes. It is necessary to add the solution of sodium nucleate to the dye, otherwise the formation of colloidal gels prevents precipitation.

Nucleic acid and tetramethyldiaminotriphenylcarbinol give a

precipitate having the composition of a tetrabasic salt,

$$C_{43}H_{57}O_{34}N_{15}P_4,4(C_{21}H_{25}N_9),9H_2O.$$
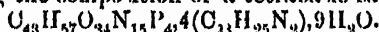
Treatment with alcohol extracts the dye, leaving a more or less colourless residue. It is considered that an ethyl ether of the dye and nucleic acid are formed.

The compound with hexamethyl-p-rosaniline is also tetrabasic, namely, $C_{41}H_{57}O_{34}N_{15}P_4,4(C_{25}H_{30}N_3),9H_2O.$ It forms a remarkable jelly during the preparation, which can be drawn out into very long threads. It is remarkable in being entirely soluble in methyl alcohol. Some decomposition takes place in alcoholic solution, part of the dye being eliminated.

The substances are considered to be chemical rather than adsorption compounds, and the whole of the phosphorus is shown to be fixed as nucleic acid.

Crystal-violet is a very suitable precipitant for nucleic acid, and may be used to purify it.

Methylene-blue gives a precipitate with nucleic acid, which is readily filtered and washed. It is entirely indifferent towards all solvents, and in no case could the dye be eliminated. E. F. A.

Preparation of an Iron Derivative of Iodoparanucleic Acid. KNOLL & Co. (D.R.-P. 258297. Compare A., 1909, i, 275).—When the iron derivative of paranucleic acid (Salkowski, A., 1901, i, 242, 434) is dissolved in 8% hydrochloric acid, and treated at 50° with a solution of iodine in potassium iodide, it furnishes the *iron* derivative of *iodoparanucleic acid*, a reddish-brown powder which has therapeutic properties and contains : iodine = 8%, iron = 13%, phosphorus = 2%, and nitrogen = 12%.

It can also be prepared from iodocaseinogen, pepsin, and a solution of iron alum ; or by the action of iodine on paranuclein in the presence of iron alum. F. M. G. M.

Action of Quinones on Wool and Other Protein Substances. WASSILI W. SCHARVIN (*Zeitsch. angew. Chem.*, 1913, **26**, 254). - Wool is dyed reddish-brown when acted on by the vapour or solutions of p-benzoquinone. Derivatives of p-benzoquinone act in a similar manner, the rate of reaction and colour depending on the compound employed; anthraquinone and phenanthraquinone are without action on wool.

Silk, leather, casein, egg-albumin, gelatin, etc., are dyed similarly by p-benzoquinone and its derivatives.

The conclusion is drawn that the quinone reacts with the amino-groups in the protein, and in the case of chloro-derivatives it is found that part of the chlorine is eliminated as hydrogen chloride, although chlorine can also be detected in wool dyed with dichloro-benzoquinones. W. H. G.

Preparation of Fibrinogen by Dialysis Against Sucrose Syrup. MAURICE PIETTRE and ANTONY VILA (*Compt. rend.*, 1913, **156**, 1182—1185).—The plasma is demineralised by dialysis against a syrup of sucrose followed by dialysis against distilled water. The

plasma, placed in a collodion bag, is first immersed in the sugar syrup for eight to ten hours, then removed, and the bag and contents placed in distilled water until the contents of the bag have returned to their original volume. By this means practically the whole of the mineral substances are removed, and the fibrinogen is deposited during the second operation, thus being isolated in the minimum of time with the use of but little liquid.   W. G.

β-Glutokyrine Sulphate. MAX SIEGFRIED (*Zeitsch. physiol. Chem.*, 1913, **84**, 288—299).—By the action of silver salts and barium hydroxide on glutokyrine a simplification of the glutokyrine molecule is brought about (compare Levene and Birchard, this vol., i, 109). There is no evidence that the silver and barium hydroxide treatment leads to a separation of the constituents of a mixture of kyrines. The quotient CO_2/N becomes smaller after treatment, but there is no increase in the nitrogen measured by Sörensen's formaldehyde method, indicating that no peptide linkings have been destroyed. On hydrolysis of the various fractions obtained during the treatment, arginine and lysine were obtained.   E. F. A.

The Rate of Destruction of Pepsin by the Direct Electric Current. W. E. BURGE (*Amer. J. Physiol.*, 1913, **32**, 41—43).— The digestive activity of a solution of pepsin is decreased (as is that of ptyalin) by the passage through it of a direct electric current at a uniform rate per unit of current.   W. D. H.

A New Method of Isolating Trypsin. HENRY LEOPOLD HOLZBERG (*J. Biol. Chem.*, 1913, **14**, 335—339).—The addition of safranine to aqueous solutions of Grübler's or Fairchild's trypsin, or to aqueous extracts of the pancreas causes a precipitate which is strongly proteolytic. The precipitate contains safranine, and is sparingly soluble in water. Removal of the safranine, or an increase in water solubility has not yet been accomplished. The precipitates produced by alcohol, or by a mixture of alcohol and ether in the mother liquor are practically devoid of proteolytic activity.   W. D. H.

The Enzymes of the Pancreas. II. The Action of Calcium Salts in the Generation of Trypsin from Trypsinogen. JOHN MELLANBY and V. J. WOOLLEY (*J. Physiol.*, 1913, **46**, 159 -172).— Salts of barium and strontium activate pancreatic juice as effectively as salts of calcium. On the addition of these salts to the juice the carbonate is precipitated, and the inhibiting alkali (sodium carbonate) is thus removed; the enterokinase (which is always present in the juice, although in variable amounts) is then allowed to act and convert trypsinogen into trypsin.   W. D. H.

Action of Ammonia on Invertase. IV. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **84**, 408—416. Compare this vol., i, 113, 541).—Invertase takes up rather more dry ammonia than diastase. Some of the ammonia is not removed in a vacuum, and nitrogen determinations indicate that part has combined with some constituent

of the enzyme. The treatment does not affect the activity of the enzyme, but after the removal of the ammonia in a vacuum the activity is less, indicating that some such chemical process as the formation of an anhydride is concerned. The conclusion is drawn that the presence of free carboxyl groups is necessary for the enzyme activity. The mere addition of ammonia to form ammonium salts and aldehyde additive compounds has no effect on the specific activity. There is thus a difference in the active chemical groups in diastase and invertase as already indicated in the experiments (*loc. cit.*) with anhydrous hydrogen chloride. E. F. A.

Synthetical Properties of Emulsin. VERNON K. KRIEBLE (*Biochem. Bull.*, 1913, **2**, 227).—An emulsin which produced *l*-mandelonitrile from amygdalin, two years later produced the *d*-variety. This is explained by the supposition that the fresh emulsin contains two enzymes, one of which synthesises the *d*-nitrile from benzaldehyde and hydrocyanic acid, whilst the other, which is less stable, synthesises the *l*-nitrile. Fresh emulsin from sweet almonds produces the *l*-, and from bitter almonds the *d*-nitrile. W. D. H.

The Biochemical Synthesis of β-Methylglucoside in a Neutral Liquid, not Participating in the Reaction. ÉMILE BOURQUELOT and ÉM. VERDON (*Compt. rend.*, 1913, **156**, 1264—1266; *J. Pharm. Chim.*, 1913, [vii], **7**, 482—486).—Emulsin, although insoluble in acetone, will bring about the synthesis of β-methylglucoside by its action on a solution of dextrose and methyl alcohol in acetone containing 20% of water. This synthesis in acetone solution is as complete as in alcoholic solution, but is somewhat slower at first. Thus the ferment is capable of synthesising and hydrolysing glucosides in a neutral liquid, such as acetone, in which it is completely insoluble (compare A., 1912, i, 593). W. G.

The Enzymes of the Character of Emulsin. LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1913, **50**, 486—496).— Adopting Euler's suggestion as to nomenclature, the enzyme which brings about the hydroxynitrile synthesis is termed the *oxynitrilese*, whereas that which causes the scission of the former substance is called the *oxynitrilase*. The conclusion is drawn that oxynitrilese is not identical with δ-emulsin (amygdalase + prunase), because (1) a preparation which has been heated for some time at 40° can still cause the synthesis of an optically active nitrile, whereas it does not lead to the decomposition of amygdalin. (2) A preparation which has been treated successively with acid and then with alkali (to neutralise the acid) behaves in a similar way. (3) Filtrates from the precipitates produced by copper sulphate, by saturation with magnesium sulphate or half-saturation with ammonium sulphate, produce no synthetic action, although they exert the degrading action. The experiments on which these conclusions are founded did not, however, always yield concordant results. The conclusion is also drawn that oxynitrilase and oxynitrilese are different. The grounds are (1) that the latter is more rapidly inactivated by the action of benzaldehyde cyanohydrin,

(2) In several fruits of Umbelliferæ, only the oxynitrilase is present. (3) Preparations can be artifically obtained which contain only the oxynitrilese.   S. B. S.

Reversible Enzyme Action. Hydrolysis and Synthesis of Fats by a Lipase. UGO LOMBROSO (*Chem. Zentr.*, 1913, i, 1043—1044; from *Arch. Farmacol. sperim.*, 1912, **14**, 429—459).— Pancreatic secretion and intestinal juice were used as sources of lipase. At 37° hydrolysis of fats sets in immediately and continues until 80% has been changed. Synthesis is slow, requiring thirty to forty hours before it can be detected, and the amount is extremely small. The addition of bile had not the slightest effect on the synthetic process, but it accelerates the hydrolytic changes. Prolonged heating at 40° damages the hydrolytic enzyme, but does not affect the synthetic. Glycerol lessens the destructive influence of heat, but oleic acid has no such influence. The synthetic enzyme in the pancreas is not favoured by prolonged contact with either glycerol or oleic acid before these are mixed Pancreatic juice preparations which contain the synthetic enzyme have only feeble lipoclastic properties. The addition of fats retards the synthetic changes, but does not stop them. Intestinal secretions which are active hydrolytically have no synthetic activity.
                                                        E. F. A.

Enzyme Action. V. Action of Neutral Salts on the Activity of Castor Bean Lipase. K. GEORGE FALK (*J. Amer. Chem. Soc*, 1913, **35**, 601—616. Compare Falk and Nelson, A., 1912, i, 522, 593 ; Falk and Hamlin, this vol., i, 303 ; Falk, this vol., i, 433)—An account is given of experiments to determine the influence of neutral salts on the activity of a castor bean lipase preparation towards ethyl butyrate. In all cases, the change in the activity was found to be a continuous function of the concentration of the added salt. The activities, as compared with those of pure aqueous solutions, were decreased by the uni-univalent salts, by the chlorides and nitrates of barium and calcium (except for dilute solutions) and magnesium, by sodium oxalate, and by dilute solutions of sodium sulphate. The activities were increased by dilute solutions of the chlorides of barium and calcium, by concentrated solutions of sodium sulphate, by magnesium sulphate, and by manganous chloride and sulphate. Potassium sulphate solutions did not affect the activity.

The retarding action is probably due to coagulation of the enzyme by the salts, the ions of which produce their individual specific effects in each case. The accelerating action cannot be so easily explained, except perhaps for cases in which an increased formation of active lipase may be assumed (compare Falk and Hamlin, *loc. cit.*).   E. G.

Enzyme Action. VI. Specificity of Lipase Action K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1913, **35**, 616—624)—An account is given of the effect of methyl and ethyl alcohols, acetone, glycerol, and dextrose on the activity of a preparation of lipase from the castor bean. Solutions of the alcohols and acetone exerted an inhibiting action on the hydrolysis of ethyl butyrate, the effect increasing with the con-

centration, but solutions of glycerol and dextrose did not produce any inhibiting effect except perhaps in concentrated solutions. It is considered probable that the simpler esters exert a specific inhibiting action on the activity of lipase similar to that exerted by the simpler alcohols, and that higher esters exert a smaller inhibiting action like that exerted by glycerol. This view is in harmony with the results obtained on testing the activity of castor bean lipase with solutions of methyl and ethyl acetates, ethyl butyrate, and glyceryl triacetate. In the light of these results, glyceryl triacetate is regarded as the most suitable ester for testing lipolytic activity.   E. G.

Enzyme Action. VII. Further Study of the Hydrolytic Action of Amino-acids on Esters. MARSTON LOVELL HAMLIN (*J. Amer. Chem. Soc.*, 1913, **35**, 624—632).—In continuation of the study of the hydrolytic action of certain amino-acids on esters (Falk and Nelson, A., 1912, i, 593) it has been found that glycine, glutamic acid, and aspartic acid exert a varying action on methyl and ethyl acetates, glyceryl triacetate, phenyl acetate, ethyl butyrate, and ethyl and phenyl benzoates. If these esters are arranged in the order of decreasing amounts of hydrolysis, the order varies with the hydrolytic agent used, namely, water, glycine, or glutamic or aspartic acid, and this indicates that the action is selective. Solutions containing both glycine and acetic acid exert a smaller hydrolytic action on methyl acetate and ethyl butyrate than do solutions of acetic acid alone.
                                                                      E. G.

Preparation of Thrombokinase from Fibrin. H. L. F. BOSWELL (*Proc. Physiol. Soc.*, 1913, iii; *J. Physiol.*, **46**).—Distilled water extracts thrombokinase from washed fibrin, but not thrombin.
                                                                      W. D. H.

Glyoxylase. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, **14**, 423—431).—The catalyst, *glyoxylase*, studied converts methylglyoxal into lactic acid, and phenylglyoxal into mandelic acid. Evidence is presented that the agent is an enzyme; it is contained in aqueous extracts of muscle, liver, blood corpuscles, yeast cells, and the tissues of the oyster, but not in serum, potatoes, or cultures of the *B. bulgaricus*. The acids yielded are mixtures of the lævo- and inactive forms. It is possible that more than one enzyme is concerned.
                                                                      W. D. H.

Compounds of Carboxyarylarsinic Acids with Amino-acids Derived from Proteins. Hippuroarsinic Acid. LOUIS HUGOUNENQ and ALBERT MOREL (*J. Pharm. Chim.*, 1913, [vii], **7**, 383—389).—Hippuroarsinic acid and arsenohippuric acid have been prepared, and their physiological actions compared with those of benzarsinic acid and arsenobenzoic acid.

Dichloroarsinobenzoyl chloride (Fournean and Oechslin, A., 1912, i, 928) reacts with glycine in presence of *N*-sodium hydroxide solution to give a liquid from which, on addition of hydrochloric acid, hippur-

aisine oxide is precipitated along with some benzarsine oxide. This precipitate on solution in sodium hydroxide solution is oxidised by hydrogen peroxide to a mixture of benzarsinic and hippuroarsinic acid and the former is precipitated completely on adding hydrochloric acid in excess. The filtrate is made alkaline and concentrated under reduced pressure. On adding alcohol there separate *trisodium hippurarsinate*, $Na_2AsO_3 \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Na,4H_2O$, which crystallises from alcohol in needles, and on treatment with alcohol and hydrochloric acid furnishes crystalline *hippurarsinic acid*,

$$H_2AsO_3 \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H,$$
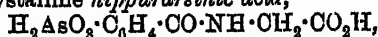
which is very soluble in water, but like the analogous substances decomposes when its aqueous solution is boiled with calcium or barium chloride or magnesia mixture. On reduction by Ehrlich and Bertheim's method, it yields *arsenohippuric acid*,

$$CO_2H \cdot CH_2 \cdot NH \cdot CO \cdot C_6H_4 \cdot As:As \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H,$$
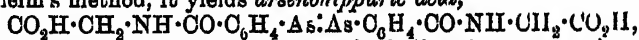
a yellow powder, soluble in solutions of alkali carbonates or phosphates, forming unstable solutions, which deposit highly toxic arsine oxides, but gives solutions in alkali hydroxides, which are stable in the absence of air, and have a toxicity similar to those of solutions of arsenobenzoic acid.   T. A. H.

Physiological Chemistry.

Calorimetrical Experiments on Warm-blooded Animals. ARCHIBALD V. HILL and (MISS) A. M. HILL (*J. Physiol.*, 1913, 46, 81—103).—An automatic self-registering respiration calorimeter for small, warm-blooded animals is described; by its use it is possible to estimate within 2% the total heat liberated. In fasting rats at 15°, the heat production per gram is constant if the animals are more than one-third the size of the full-grown animal; for smaller specimens the figure rises rapidly, and may reach 70% greater than for grown animals. If the body surface is S, and the weight H, then in rats, $S = 10 \times W^{2/3}$. The rate of heat production to S during inanition is not constant, being 140 cal. per sq. cm. for small animals, 99 for medium-sized, and 110 for large animals. Any assumption that heat production is determined by heat loss is therefore unjustifiable. The high value in small animals is probably not due to their smallness, but to their youth, and consequently high chemical activity. Rats fed on biscuit at 15° give out 13% more heat than when fasting. If this is due to Rubner's specific dynamic value of foodstuffs, it suggests that the animals, even when fasting, give out more heat than is necessary to keep them warm. If the animals are kept in the calorimeter in groups, the heat production is lessened, because contact prevents heat loss, and especially as company promotes sleep and rest; they certainly grow faster.   W. D. H.

Oxygen Capacity of the Blood Pigment. WILHELM MANCHOT (*Zeitsch. physiol. Chem.*, 1913, **84**, 306—308).—Polemical. A reply to Burn (this vol., i, 306) and to Butterfield (A., 1912, ii, 820).

E. F. A.

The Phosphorus content of the Blood of Normal and Parathyroidectomised Dogs. ISIDOR GREENWALD (*J. Biol. Chem.*, 1913, **14**, 369—379).—After removal of the parathyroid glands, the total phosphorus of the blood and serum is increased, even at a time when the tremors are slight. The increase may be as much as 160 mg. of phosphorus per kilo. of blood. The greater part of this increase is in the fraction which is insoluble in the usual lipoid solvents, but is soluble in a mixture of dilute hydrochloric or acetic and picric acids.

W. D. H.

Formation of Lactic Acid from Dextrose, Glyceraldehyde, and Dihydroxyacetone in the Blood of the Ox and Pig. ADAM LOEB (*Biochem. Zeitsch.*, 1913, **50**, 450--456).—The red corpuscles of the ox and pig, which do not cause glycolysis of either the blood-sugar or added sugar, and only produce a small amount of lactic acid, nevertheless show either as high (pig) or even a higher (ox) capacity for producing lactic acid from glyceraldehyde than the blood of the dog, which has considerable glycolytic action. The red corpuscles of the pig have, furthermore, a considerably greater capacity than those of either the dog or ox of converting dihydroxyacetone into lactic acid.

S. B. S.

The Formation of Lactic Acid from Carbohydrates in Laked Blood. WALTER GRIESBACH (*Biochem. Zeitsch.*, 1913, **50**, 457—466).—From the blood of the ox and dog, cell-free blood solutions can be obtained, which, while they do not act on dextrose, can convert *dl*-glyceraldehyde and dihydroxyacetone into lactic acid as vigorously as the intact corpuscles. A mixture of racemic and *l*-acids is thereby produced, as is the case when the intact corpuscles are employed. The conclusion is drawn that the degradation of sugar into lactic acid takes place in two phases, and by two ferments; in the one phase the conversion of the dextrose into glyceraldehyde takes place, and this action is only possible when the cells are intact; in the second phase, the aldehyde is converted into lactic acid, and for this process the intact cell is not necessary.

S. B. S.

The Estimation of the So-called "Residual Reduction" of the Blood. PAUL MAYER (*Biochem. Zeitsch.*, 1913, **50**, 362--368).—By "residual reduction" is meant the reduction of Fehling's solution after the sugar in the blood has been removed by fermentation with yeast. It is now shown that pure dextrose solutions (0·1%), after treatment with various races of pure yeasts, also show a "residual reduction," after removal of proteins, etc., by colloidal iron hydroxide. This is due to substances derived from the yeast itself, and the concentrated solutions, after treatment, show reactions for amino-acids and, in most cases, also for purine substances.

S. B. S.

The Formaldehyde Titration of Proteins. II. FRIEDRICH OBERMAYER and ROBERT WILLHEIM (*Biochem. Zeitsch.*, 1913, **50**, 369—385. Compare A., 1912, ii, 399).—It is possible, by Sörensen's method, to estimate the reactive amino-groups in a protein, and the ratio of this reactive amino-nitrogen to the total nitrogen is designated the "amino-index." In euglobulin the mean value (21·5) of the index is higher than that of albumin (about 12). In mammals the value for pseudoglobulin is about the same as that for euglobulin, but in birds it does not differ very much from that of albumin (the mean value is about 15). By means of the determination of this index it is possible to show that the various protein fractions of serum are not homogeneous substances. It is also possible to demonstrate differences in the sera of different species, and the fraction salted out by 25—30% ammonium sulphate has a higher "amino-index" in the case of a hen (28·5- -32·5) than in the case of an ox (19—21·5). The serum of the horse is similar to that of the ox, and the serum of the goose is similar to that of the hen; it is therefore possible that the "amino-index" of a definite fraction may be characteristic for definite classes of animals.

S. B. S.

The Specificity of Immunity Reactions, and their Explanation as Colloidal Chemical Phenomena. KURT LANDSTEINER (*Biochem. Zeitsch*, 1913, **50**, 176—184).—The author does not regard the contention of Michaelis and Davidsohn (this vol., i, 121), that certain immunity reactions are not of colloidal chemical character, as justified. The view was arrived at on the ground that certain precipitin reactions are independent to a large extent of the hydrogen ion concentrations. Attention is especially called to the fact that serum, blood corpuscles, etc., of different species exert the maximum action in the presence of different hydrogen ion concentrations. This point is illustrated by the adsorption of ricinus agglutin, by the different strengths of acid or alkali which haemolyse the corpuscles, by the differences in the agglutination of stromata, and the differences in the precipitability of the sera precipitating reagents.

S. B. S.

The Coagulation of the Blood. The Significance of Various Physico-chemical Processes in the Action of Thrombin. M. LANDSBERG (*Biochem. Zeitsch.*, 1913, **50**, 245 272). The temperature curve of reaction velocity of blood coagulation is the result of at least two concurrent processes. The main process is the reaction between the thrombin and fibrinogen, and is apparently of a chemical character. The other reaction, which is antagonistic to the first, is an inhibition of the thrombin action due to its adsorption by the proteins of the serum. Both processes are accelerated by increase of temperature, which exerts therefore a twofold influence on the clot formation. The temperature curve depends to a large extent on the conditions of the experiment. In such combinations, in which the adsorption process is reduced to a minimum, the clotting reaction resembles a fermentative process with an optimal temperature of 35—40°. In the combination,

magnesium sulphate plasma-| Schmidt's thrombin, which is particularly favourable to adsorption processes, there is a diminution of the reaction velocity even at 17– 20°. The adsorption of thrombin by the serum proteins increases with temperature, and is only partly reversible. The conversion of the serum thrombin into its inactive "metathrombin" form is simply due to adsorption; the reactivation by Schmidt's method by means of alkalis being simply the breaking down of the adsorption compound. The general results indicate that there are no facts which are antagonistic to the idea of a fermentative process in clotting.

<div style="text-align: right">S. B. S.</div>

Water Drinking. XIV. The Digestive Efficiency of Saliva as Increased by Dilution with Water. OLAF BERGEIM and PHILIP B. HAWK (*J. Amer. Chem. Soc*, 1913, **35**, 461—476).—Mattill and Hawk (A., 1912, ii, 65) have shown that the drinking of large volumes of water with meals increases the amount of carbohydrate digested. Experiments which have now been made *in vitro* show that the dilution of normal human saliva increases its digestive efficiency. The optimum dilution depends on the nature of the diluent, and is 4 volumes for 0·3% sodium chloride solution and 7 volumes for water. Water, softened by the addition of lime water, exerts an inhibiting effect, due principally to the presence of magnesium hydroxide.

<div style="text-align: right">E. G.</div>

The Action of Sugar on Digestion. ERWIN THOMSEN (*Zeitsch. physiol. Chem.*, 1913, **84**, 425—436) —Sucrose has no direct action on the stomach, or on the secretion of pancreatic juice and bile. Its action on the small intestine is due to prolongation of gastric digestion without altering the secretions. The lengthening of gastric digestion is due to the occurrence of long pauses in the emptying of the stomach. Sucrose is completely or almost completely absorbed in the small intestine in large quantities, but it delays the absorption of the chyme.

<div style="text-align: right">W. D. H.</div>

The Pepsin-Chymosin Question. A. RAKOCZY (*Zeitsch. physiol. Chem.*, 1913, **84**, 329—353. Compare A., 1911, i, 827). The question of the identity of the milk coagulating and protein digesting enzymes is bound up with nature and age of the animal. Hasselt (A., 1911, i, 248), Porter (A., 1911, i, 698), and Burge (A., 1912, i, 148) have all established the presence of a special milk coagulating enzyme in the stomach of the calf. In such infusions where the two enzymes are present they can be separated by Hammarsten's casein method, but with the stomach infusions from other animals which contain no chymosin no such separation could be effected. The power of coagulating milk is inseparably bound up with the peptic enzyme.

In a similar manner elastin may be used to adsorb pepsin, whereas it has no effect on chymosin. This method enables the two enzymes to be separated in the gastric juice of the calf, but not in that of other animals. In slightly acid solution (*N*/200 hydrochloric acid) edestin adsorbs chymosin, but there is no action when the acidity

is increased ($N/80$-acid).   On digestion with water, the adsorbed chymosin is recovered from the edestin.

Pepsin in the ox and in the calf appears to have the same properties, and that derived from the two sources is the same.

Milk is coagulated in the stomach in all mammals from the first day of life onwards.   The ruminants and such animals as the horse and the pig secrete both pepsin and chymosin.   Human beings secrete pepsin only, whilst in dogs and cats neither pepsin nor chymosin is present, and the coagulation is due to other factors which are at present but imperfectly understood.   E. F. A.

Formation of Plastein. I. P. GLAGOLEV (*Biochem. Zeitsch.*, 1913, **50**, 162—175).—Formation of plastein has characteristics of a fermentative character, in that it takes place in the presence of minute quantities of the digestive fluid, requires a certain definite reaction of the medium, and does not take place if the digestive fluid is first boiled.   It appears to be a generative process, in that when produced by rennin powder (Witte's), natural gastric juice, or papayotin, there is a diminution of the reactive amino-groups, as determined by Sörensen's formaldehyde titration.   Plastein formation is a reversible process, and depends on the quantities of ferment, concentration of reacting substances, and reaction of the medium.   The reversibility of the reaction can even be detected in very concentrated syrupy solutions.   S. B. S.

Synthetic Powers of the Organism of the Dog. WILHELM STEPP (*Zeitsch. physiol. Chem.*, 1913, **84**, 359—360.   Compare A., 1911, ii, 1002; this vol., i, 419).—This is a reply to Abderhalden's criticism of the author's work.   The death which follows feeding mice on nutriment boiled in alcohol is attributed to destruction of lipoids, and doubt is expressed whether mice possess the synthetic powers to construct these substances from simple cleavage products.
W. D. H.

Metabolism Experiments on Parathyroidectomised Dogs. ISIDOR GREENWALD (*J. Biol. Chem.*, 1913, **14**, 363—367)—After removal of the parathyroids, the excretion of phosphorus in the urine is lessened; there is no increase of phosphorus in the fæces; apparently it is retained in the body.   This retention appears to be primary, and not secondary to the retention of sodium or potassium, or of both.   In no experiments did the retention of the bases precede that of phosphorus.   Whether the changes are the cause of tetany is questionable.   W. D. H.

The Carbohydrate-sparing Action of Alcohol. O. TUGEL, E. BREZINA, and ARNOLD DUBIG (*Biochem. Zeitsch*, 1913, **50**, 296—345).—The method of experiment was as follows.   A human subject was kept on a carbohydrate-rich diet.   A large quantity of dextrose or lævulose was then ingested, and the respiratory quotient was determined at definite intervals afterwards, while the subject was kept in a state of rest.   The results thus obtained were com-

pared with those where the experiment was carried out in a similar manner, but where alcohol was ingested in addition to a carbohydrate. After ingestion of 100 grams of dextrose, it was found that the respiratory quotient sank at first, but began to rise after half an hour, until after two hours it gradually rose to 1. After an interval, it gradually sank, until after four hours it reached the original value. Repeated doses of 100 grams of dextrose administered to a subject on carbohydrate-rich diet finally caused only a slight rise in the respiratory quotient. The sugar in this case was neither burnt, excreted as such, nor found in the blood-stream. Lævulose acted in a similar manner, but the action was somewhat more marked than that of dextrose. By repeated doses of 30 grams of lævulose, the respiratory quotient could be maintained for a long time at 1. The general effect of the ingestion of alcohol with the sugar was to depress the respiratory quotient as compared with the control experiments without alcohol. The addition caused no change in the calories used up. In the first period, it was calculated that 70—100 mg. of alcohol were burnt per minute. The depression of the respiratory quotient is not due to the narcotic action of the alcohol, as this is uninfluenced by other narcotics, such as opium. The conclusion is therefore drawn that alcohol exerts a carbohydrate-sparing action in the metabolism.

S. B. S.

Nitrogenous Metabolism. EMIL ABDERHALDEN and ARNO E. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, **84**, 361—362).—Polemical. A reply to Grafe (this vol., i, 547). W. D. H.

Intermediary Metabolism of Amino-acids. HENRY D. DAKIN (*J. Biol. Chem.*, 1913, **14**, 321—333).—Serine, cysteine, proline, ornithine, and arginine all yield large amounts of sugar in glycosuric dogs. Valine, leucine, isoleucine, lysine, histidine, phenylalanine, and tryptophan yield little or no sugar. Arginine is thus the only amino-acid with more than five carbon atoms which yields sugar, and in this case the ornithine moiety is responsible for the action. Amino-acids with branched chains yield little or no sugar. Proline is the only cyclic amino-acid which yields sugar readily; the opening of the ring is the first step in the breakdown. Phenylalanine, tyrosine, and tryptophan all contain an alanine side-chain, but yield no sugar, although alanine itself does; this indicates that the side-chain is broken up.

Ornithine, lysine, arginine, proline, tryptophan, and di-iodo-tyrosine do not yield acetoacetic acid in marked amounts when added to blood perfusing a dog's liver. W. D. H.

The Behaviour of Some Hydantoin Derivatives in Metabolism. II. 2-Thiohydantoins. HOWARD B. LEWIS (*J. Biol. Chem.*, 1913, **14**, 245—256).—2-Thiohydantoin is toxic for rabbits; the toxicity is increased by the substitution of an alkyl group in the 4-position. 2-Thio-4-methylhydantoin is less toxic, and 2-thio-hydantoin-4-acetic acid is not toxic in doses of 2 grams. 2-Thio-

4-methylhydantoin in fatal doses causes albuminuria in rabbits. The sulphur is not oxidised.   W. D. H.

Purine Metabolism. I. Uricolysis in the Human Subject. ALONZO E. TAYLOR and WILLIAM C. ROSE (*J. Biol. Chem.*, 1913, 14, 419—422).—The nitrogen of milk and eggs was replaced by that in sweetbreads. The purine nitrogen of the urine was increased; this increase is due solely to uric acid. More than half the ingested nitrogen was, however, either destroyed in the alimentary tract before absorption, or was converted in metabolism into non-purine substances, presumably urea.   W. D. H.

The Utilisation of Ammonia in Protein Metabolism. ALONZO E. TAYLOR and A. I. RINGER (*J. Biol. Chem*, 1913, 14, 407—418. Compare this vol, i, 548).—In dogs during inanition, and still more in diabetic dogs, ammonium carbonate given by the mouth led to a retention of nitrogen; given under the skin it was promptly eliminated. The administration of urea was followed by complete elimination of all the nitrogen. Ammonia given to man on a protein-free diet was retained to the extent of two-thirds. The presence of carbohydrates in the food is not a necessary factor in the retention of nitrogen from ammonia. It is suggested that the nitrogen is retained because of a reversible reaction that leads to combination with the α-ketonic- or α-hydroxy-acids to form amino-acids, which may be used in the synthesis or sparing of the body proteins.   W. D. H.

The Action of Completely Cleaved Nutriment on the Alimentary Canal. OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1913, 84, 419—424).—Although it has been shown that animals can maintain nitrogenous equilibrium on protein food which is broken down to the simplest constituents, no note has hitherto been made on the effect of such diet on the alimentary canal itself. There are other factors, such as taste, consistence, etc., which influence digestion in addition to chemical composition. In the present research, however, in a dog with a duodenal fistula fed on two commercial specimens of such nutriment (erepton and hapan), no effect on the time of digestion in the stomach or on the amount of digestive juices secreted could be found, when compared with what occurs on a usual diet. These preparations were found to be well absorbed when administered by the rectum.   W. D. H.

The Preparation of Dry Animal Organ Material. ALBRECHT KOSSEL (*Zeitsch. physiol. Chem.*, 1913, 84, 354—358).—An elaborate apparatus is described which enables animal organs to be frozen solid by means of carbon dioxide snow, cut into small pieces, and dried below 0°. Colourless or reddish-grey powders are thus obtained from the original organs.   E. F. A.

The Relative Influence of Weak and Strong Bases on the Rate of Oxidations in the Unfertilised Egg of the Sea Urchin. JACQUES LOEB and HARDOLPH WASTENEYS (*J. Biol. Chem.*, 1913, 14, 355—362).—Weak bases, which are more efficient in causing

artificial parthenogenesis, are also more efficient in raising the rate of oxidation in the unfertilised egg-cell. This lends support to the view that bases cause parthenogenesis by accelerating oxidation.

W. D. H.

Chemistry of Embryonic Growth. I. Certain Changes in the Nitrogen Ratios of Developing Trout Eggs. Ross A. GORTNER (*J. Amer. Chem. Soc.*, 1913, **35**, 632—644).—An account is given of a study of the nitrogenous constituents of trout eggs at various stages of development. It is probable that the egg does not lose any nitrogen before hatching, but afterwards it suffers a rapid loss, until in twenty-one days after hatching, 21·96% of the total nitrogen has disappeared. During its development into the fish, the egg loses 25·35% of its weight, of which 37·26% is due to non-protein matter (fats, etc.) and 62·74% to proteins, and simultaneously basic forms of nitrogen increase at the expense of the monoamino-acids. Urea and uric acid are not produced in any considerable quantity. The composition of the nitrogenous substances which disappear indicates that there is a selective utilisation of the nitrogen compounds by the developing fish. It is probable that some of the energy of development is derived from the shifting of the nitrogen ratios, and it is suggested that as the change from monoamino-acids to basic nitrogen compounds proceeds the energy relations may perhaps be changed and heat liberated.

E. G.

Chemical Differentiation of the Central Nervous System. I. Comparison of the Brain of the Albino Rat at Birth with that of the Fœtal Pig. (Miss) MATHILDE L. KOCH (*J. Biol. Chem.*, 1913, **14**, 267—279).—Estimation of the constituents of the brain of the rat at birth shows it to be as chemically undifferentiated as the brain of a 50—100 mm. length fœtal pig. The correspondence is further supported histologically. If the nervous systems are assumed to be in corresponding states when motor control is obtained, and Donaldson's law is correct that the nervous system is in the same state at corresponding physiological ages, then the brain of the rat at birth should correspond chemically with the 100 mm. fœtal pig brain. This was found to be the case. W. D. H.

Chemical Differentiation of the Central Nervous System. II. A Comparison of Two Methods of Preserving Nerve-tissue for Chemical Examination. WALDEMAR KOCH and (Miss) MATHILDE L. KOCH (*J. Biol. Chem.*, 1913, **14**, 281—282).—The material was placed directly in 95% alcohol, and part was dried at 95°. The latter process was found to seriously affect the analyses, the most important change produced being a destruction of phosphatides; this was more marked in brains than in spinal cords. W. D. H.

Distribution of Nerves in the Heart. (Miss) WINIFRED C. CULLIS and (Mrs.) ENID M. TRIBE (*J. Physiol.*, 1913, **46**, 141—150). --After section of the auriculo-ventricular bundle in rabbit and cat,

pilocarpine and muscarine no longer inhibit ventricular activity; they act on the auricles as usual, and are antagonised by atropine; atropine has no effect on the ventricles. Under similar conditions adrenaline produces its normal augmentor effect on the ventricles. From this, it appears that the ventricle does not receive vagus fibres, and that the normal effect of the vagus on the ventricles is therefore indirect through the auricle; further, the ventricle must be supplied with sympathetic fibres, which reach it not only by way of the auriculo-ventricular bundle.   W. D. H.

Action of Certain Drugs on Isolated Strips of Ventricle. (Miss) Constance Leetham (*J. Physiol.*, 1913, **46**, 151—158).— Experiments are recorded with isolated strips of ventricle which confirm the findings of Cullis and Tribe (see preceding abstract).
                                        W. D. H.

Action of Dyes on the Isolated Frog's Auricle. A. J. Clark (*Proc. Physiol. Soc*, 1913, xx; *J. Physiol.*, **46**).—The excised auricle and fibres of the frog's heart beat in Ringer's fluid for some hours. Neutral-red dissolved in the fluid stains the muscular fibres red, but does not injure them. If the alkalinity of the fluid is increased, the fibres remain red as long as they exhibit activity, but when the concentration of alkali is sufficient to arrest activity, they turn yellow. This agrees with Warburg's observations on sea-urchin eggs, and supports the conclusion that normally animal cells are not permeable to hydroxyl ions.   W. D. H.

The Presence of Trimyristin and Cephalin in the Liver. Armando Frank (*Biochem. Zeitsch.*, 1913, **50**, 273—282).—The coagulated and dried ox-liver was extracted by acetone, from which solution, on keeping, a crystalline substance separated, which was identified as trimyristin. The liver powder was then extracted with light petroleum. The extract thus obtained was dissolved in ether and precipitated with acetone. The precipitate was redissolved, filtered, and then reprecipitated with acetone, and this procedure was repeated many times. The substance was, in composition and properties, nearly allied to the cephalin isolated from brain by Thudichum and others. Experiments were carried out which tend to show that the so-called liver jecorin is cephalin contaminated with other substances, such as sugar.   S. B. S.

Estimation of Adrenaline. Thomas R. Elliott (*Proc. Physiol. Soc.*, 1913, xv—xvii; *J. Physiol.*, **46**).—Many workers give adrenaline values which are too low owing to faulty extraction and estimation. At birth nearly all the adrenaline is in the outside paraganglia; in the adult the two suprarenals contain 8—9 mg. In septic conditions it may drop to a quarter of this value. Estimations may be made by the effect on arterial pressure, or by the new colorimetric reaction of Folin and Denis with phosphotungstic acid. The two work out practically the same, but the latter is much the simpler and quicker method.   W. D. H.

The Iodine and Phosphorus Contents, Size, and Physiological Activity of the Fœtal Thyroid Gland. FREDERIC FENGER (*J. Biol. Chem*, 1913, **14**, 397—405).—Functional therapeutic activity and the presence of iodine coincide in the fœtal human thyroid as in extra uterine life. The amount of iodine during the last three months of fœtal life is uniform in the various seasons. The fœtal thyroid is relatively large, and contains more iodine and phosphorus per unit of body weight than those from mature animals. This is especially the case for females. Enlarged thyroid glands were found in small fœtuses. The enlarged glands, as in the adult, contain less iodine and more phosphorus than the normal. Enlargement of the fœtal thyroid is common, and is probably the consequence of insufficient supply or faulty assimilation of iodine on the part of the pregnant animal. W. D. H.

The Changes in Metabolism Produced by the Extirpation of Thyroids and Parathyroids. RAFFAELE PALADINO (*Biochem. Zeitsch.*, 1913, **50**, 497—507).—The experiments were carried out on dogs. The parathyroids and thyroids appear to exert a considerable influence on the phosphorus metabolism, for after extirpation the amount of phosphate excreted (chiefly in the form of phosphates of alkaline earths) increases to three times the normal amount. The amount of calcium excreted diminishes. There is no marked change in the nitrogen excretion. S. B. S.

The Relation of the Corpus Luteum to Lactation. CHARLES H. O'DONOGHUE (*Proc. Physiol. Soc.*, 1913, vi; *J. Physiol.*, **46**).—In rabbits, if the rupture of the Graafian follicles in the ovary is followed by the formation of corpora lutea, there is also growth of the mammary glands, but there is no such growth if corpora lutea do not form. W. D. H.

Biochemistry of the Female Genitalia. III. Enzymes of Ovary, Uterus, and Bladder in Sheep. JACOB ROSENBLOOM and THUISCO A. ERPF-LEFKOVICZ (*Biochem. Bull.*, 1913, **2**, 233—235).—Lipase and amylase are more abundant in the ovary and uterine mucous membrane of pregnant than of non-pregnant sheep. Pregnancy has no effect on the acid-protease of either organ, but increases the alkali-protease. Bladder extracts contained lipase, amylase, and acid-protease, but no alkali-protease. W. D. H.

Biochemistry of the Female Genitalia. IV. Absence of Certain Enzymes from the Human Chorion. JACOB ROSENBLOOM (*Biochem. Bull.*, 1913, **2**, 236—237).—One chorion weighing 10 grams was examined. Extracts made with water and with glycerol were free from amylase, sucrase, maltase, lactase, lipase, peptidase, ereptase, acid-protease, and alkali-protease. The enzymes of the placenta are either developed later, or originate from the maternal moiety (decidua serotina). W. D. H.

The Effect of Small Variations in Concentration of Ringer's Solution on the Response of Isolated Plain Muscle. HENRY H. DALE (*Proc. Physiol. Soc.*, 1913, xix; *J. Physiol.*, **46**).—By adding

salt in small amounts to Ringer's fluid in which plain muscle (uterus) is suspended, the response of the muscle to the anaphylactic reaction and to stimulant drugs is lessened or annulled.   If the tonicity of the fluid is lowered by adding water, the responsiveness is increased.   The effects are not due to specific ionic action, but are due to alterations in osmotic pressure; solutions of non-electrolytes produce the same effects.   W. D. H.

Muscle Chemistry. VI. The Free Amino-acid Nitrogen Titratable by Formaldehyde and the Total Extractive Nitrogen in Muscular Tissue of Animals in a State of Inanition. GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1913, **84**, 243—253).—In dogs to which water only was given for periods varying from twelve to twenty-five days, there was no change in the total nitrogen of the muscles, but there was a small increase in the total extractive nitrogen and in the nitrogen of free amino-acids.   This change is not a progressive one, that is, it does not increase as the period of inanition increases.   Confirmatory experiments on the octopus are also recorded.   W. D. H.

The Lipins (Lipoids) of the Heart Muscle of the Ox. JACOB ROSENBLOOM (*J. Biol. Chem.*, 1913, **14**, 291—294).—Only about 40% of the ether and alcohol extract of heart muscle of the ox is composed of phospholipins (phosphatides), and practically no difference in this percentage was obtained on comparing the extractions carried out in the cold with those carried out at the boiling point of the solvent.   W. D. H.

Origin of Fatigue. GAETANO VIALE (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 253—256).—In prolonged muscular work quantities of water are eliminated in the sweat.   This water comes from the blood, which in turn withdraws water from the tissues   When a certain point is reached, the necessary water is no longer forthcoming.   This is evidenced by decreased secretion of sweat, and by increase in the amount of sodium chloride contained in it.   The origin of fatigue is to be found in this removal of water, which causes accumulation of toxins in the blood and disturbs the heat regulation of the organism.   In agreement with other workers, the author finds a decrease in red blood corpuscles and in hæmoglobin in fatigue, and this is to be explained as being due to an accumulation of them in the organs.   R. V. S.

The Behaviour of the Creatine of Muscle during Fatigue. VITTORIO SCAFFIDI (*Biochem. Zeitsch*, 1913, **50**, 402—417).—In the muscular tissue of the frog and dog (and probably in all muscular tissue) creatinine does not exist as such in a preformed condition. Care must be taken to exclude high temperatures and acids in the process of its extraction from the tissues.   Neither does creatinine appear to be formed in frog's muscle during work; if it is formed, it is either immediately removed or destroyed.   Creatine shows certain variations in the quantity found, both in resting and

fatigued conditions, these variations being of about the same order of magnitude in both cases. It was not possible therefore to draw the conclusion that the creatine is formed as a result of work. It is, however, possible that during work creatine is used up, and new supplies are formed from degradation products of the muscle proteins. The condition of the circulation exerted no influence on the creatine metabolism in the frog during muscular work, as similar results were obtained when the circulation was intact, or entirely excluded.   S. B. S.

The Effect of Adrenal Secretion on Muscular Fatigue. WALTER B. CANNON and L. B. NICE (*Amer. J. Physiol.*, 1913, **32**, 44—60).—The experiments were performed on cats, rabbits, and dogs; a fatigue curve of a voluntary muscle was obtained by stimulating its nerve. Excitation of the splanchnic nerve increased the height of the muscular contraction. The question was whether this was due to the pouring out of adrenaline into the circulation, and this is answered in the affirmative; the adrenaline appears to act, however, not on the muscle directly, but by improving the circulation of blood through it. Previously reported favouring effects of adrenaline on voluntary muscles (mainly studied in cold-blooded animals) are capable of a similar explanation.
                                                                  W. D. H.

The Consumption of Fats in the Animal Organism. G. LAFON (*Compt. rend.*, 1913, **156**, 1248—1250).—In order to determine the consumption of fat by the tissues, the author has estimated the amount of fat in the arterial blood and in the venous blood coming from the muscle, first in a state of repose, and then during activity. This has been done in the case of the horse and the ass, working on the muscle of the upper lip, activity being produced by mastication, and in the case of the dog on the muscle of a hind limb, the muscle being electrically excited. The results show that the fat is consumed directly, and to the same extent as dextrose, during the activity of the tissues, and in particular during muscular work. Muscles fatigued by electrical excitation contain less fat than fresh muscle.   W. G.

Fluorine in the Animal Organism. I. Skin and its Appendages. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1913, **156**, 1347—1353).—Fluorine is to be found everywhere in the organs of plants and animals, but is specially concentrated in a few of them. This paper gives an account of the quantitative examination for fluorine of the skin, and such appendages as the hair, epidermis, nails, tooth enamel, etc., in the case of human beings, animals, birds, and fishes. In their fluorine content, the hair, down, fish-scales, nail, and tortoise-shell resemble the epidermic tissue, whilst the enamel of teeth and the horns differ from it widely, the former parts being rich and the latter poor in fluorine. The fluorine in skin itself appears to accompany the phosphorus and increase with it, for the same organs, without being proportional

to it. It is more abundant at the adult age in human than in animal skin, and diminishes in organs which are in process of decay, such as hair, teeth, etc., of old animals.

The method of estimation consists in incinerating the organ under examination, when dried, with 1 to 1·5% of calcium oxide, and the fluorine is estimated in the alkaline non-fused ash by a method already described (compare A., 1912, ii, 681, 805, 806).   W. G.

The Relation of Osmotic Pressure to Absorption Phenomena in the Dog-fish. G. G. SCOTT and WILLEY DENIS (*Amer. J. Physiol.*, 1913, **32**, 1—7).—Dog fishes, of which the spinal cord was largely destroyed, were immersed in various solutions (methylene-blue, boric acid, potassium iodide), and the material being prevented from entering the alimentary canal, the time was noted when they appeared in the blood, urine, etc. The gill membranes appear to be the main channel of absorption, and the physical laws of diffusion suffice to explain the results.   W. D. H.

The Action of Ultra-violet Rays on the Ear of the Rabbit Influence of Intensity. Intermittent Radiations. VENCESLAS MOYCHO (*Compt. rend.*, 1913, **156**, 1268—1271. Compare this vol., i, 424).—As the intensity of the radiation increases, the time necessary for the ear to be subjected to it, to produce visible effect, diminishes. The amount of energy necessary to produce minimum visible reaction is practically constant for intensities varying from 4 to 100. If, instead of continuous radiation, the ear is subjected to intermittent treatment, the visible effect is produced when the sum of the short radiations is equal to the continuous radiation, providing that the intervals between the application of the light do not exceed forty-eight hours.   W. G.

Chemical Studies on Rhizostoma Cuvieri. RICHARD VON ZEYNEK (*Monatsh.*, 1913, **34**, 581—621).—If a jelly-fish of the above type is removed from water, a mucous substance is exuded which contains innumerable stinging threads; it causes an intense burning when cautiously placed on the tip of the tongue. The mucous substance easily undergoes decomposition; when precipitated by ammonium sulphate and redissolved by a very weak potassium hydroxide solution, acetic acid throws down a flocculent precipitate, which dissolves readily in hydrochloric acid; when heated with this acid, a solution is obtained which reduces Fehling's solution and gives an osazone. The precipitate given by acetic acid contains no phosphorus, whilst the potassium hydroxide solution gives the biuret reaction. The stinging threads are very resistant, and contain very appreciable quantities of silicic acid. When the above mucous substance is allowed to dry on the clothes, the dust causes nasal irritation and acute catarrh, which persists for several hours. The substance to which irritation is due appears to be non-volatile; a careful examination of the mucous substance, however, revealed the presence of an alkaloidal substance.

[With F. AMESEDER.]—Specimens of the Rhizostoma were

analysed, also the water in which one had lived and parts of the organism; the results are to be seen in the original

The blue colouring matter (zoocyanin) present in *Rhizostoma Cuvieri* varies slightly in tone with the age of the specimen. The fresh aqueous extract is neutral, and the coloured substance is almost entirely precipitated by a 22—27% solution of ammonium sulphate, when it is obtained as a gelatinous mass; it was purified by washing and fractional precipitation with ammonium sulphate solution. The aqueous solution of the substance is turned brown on warming to 55° or on adding alcohol or acetone. Formaldehyde has no effect, but precipitates are obtained with phosphotungstic acid, phosphomolybdic acid, potassium bismuth iodide, potassium mercuri-iodide, and a solution of iodine in potassium iodide. It thus appears that the colouring matter is a protein substance, and the composition is in confirmation of this view. The colour was examined spectroscopically. D. F. T.

Analysis of Human Bile. JACOB ROSENBLOOM (*J. Biol. Chem*, 1913, **14**, 241—244).—An analysis of a specimen of fistula bile is given, and compared with others previously published. W. D. H.

The Physiology of Secretion in the Kidney. OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1913, **84**, 451—467).—Sodium chloride and dextrose are taken up by the surviving kidney at body temperature from solutions, and fixed in loose chemical union, which is dissolved at boiling heat. These combinations, as well as the secretion of these substances by the kidney, have a certain threshold, beneath which the kidney unites with none, and over it with considerable quantities. The chemical combination with the cell-constituents is a preliminary stage in secretion. W. D. H.

The Conditions Affecting the Formation and Excretion of Formic Acid. The Estimation of Formic Acid in Urine HENRY D. DAKIN, N. W. JANNEY, and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1913, **14**, 341—354).—The formic acid in urine is partly endogenous. The effect of a number of substances on formic acid excretion was investigated, including amino-, hydroxy-, and saturated fatty acids. Special attention is called to the effect of inanition, which greatly reduces the amount excreted. The acid is largely increased when carbohydrates are given by the mouth or subcutaneously. Protein feeding is followed by a similar but smaller increase. Formic acid is regarded as a product of the intermediary metabolism of carbohydrates and proteins.

Formic acid is estimated in urine by saturating the latter with ammonium sulphate, extracting with ether, removing the formic acid from the ether by sodium carbonate, acidifying with phosphoric acid, distilling in a current of steam, adding mercuric chloride to the distillate, and weighing the calomel formed. W. D. H.

The Excretion of Nitrogen Subsequent to Ligature of Successive Branches of the Renal Arteries. J. D. PILCHER (*J. Biol. Chem.*, 1913, **14**, 389—395).—Ligaturing half the blood

supply of both kidneys causes no noticeable disturbance in renal function. Complete ligature of one artery, and one branch of the other (that is, shutting off three-quarters of the arterial supply), results in prostration, loss of weight, and an increase of excretion of nitrogen; the animals, however, recover gradually. One quarter of the kidney tissue is therefore able to do the work of the whole.

W. D. H.

A Differential Chemical Study of Glucoses from a Case of Pancreatic Diabetes. FREDERIC LANDOLPH (*Biochem. Bull.*, 1913, **2**, 217—222).—The sugar is diabetic urine (one specimen examined) is regarded as a complex of many carbohydrates which can be separated by various treatments. Some of these are dextrin-like, and yield with phenylhydrazine "pseudo-osazones," which are resinous and have low melting points. The work is not yet completed.

W. D. H.

A Modification of Diphtheria Antitoxin. A. T. GLENNY (*J. Hygiene*, 1913, **13**, 63—67).—Evidence is adduced that diphtheria antitoxin is of two kinds, which affect two kinds of the toxin, one of which is lethal, and the other of which produces the local reaction.

W. D. H.

Presence of Propionic Acid in the Secretions of Rheumatic Persons. WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1913, **156**, 1272).—The urine of rheumatic patients, after a severe attack, has an odour recalling at the same time butyric and acetic acids, and from this urine the author has isolated propionic acid. This acid he has also found in the discharge from eczema sores of such patients.

W. G.

The Action of Nitrites on the Body Temperature of Normal Rabbits, and on those Rendered Hyperthermic by Brain Stimulation EMANUEL KRAUSS (*Arch. expt. Path. Pharm.*, 1913, **72**, 97—128).—The experiments show that nitrites, as stated by Jacobj, depress the body temperature. Further observations are necessary to explain this, and also why the inhalation of amyl nitrite acts much more markedly on rabbits in a state of hyperthermia.

W. D. H.

Action of Nitrites on the Body Temperature of Rabbits. CARL JACOBJ (*Arch. expt. Path. Pharm*, 1913, **72**, 129—152).—Nitrites given in various ways (inhalation, subcutaneously, etc.) depress the body temperature of rabbits, especially if they are rendered hyperthermic by stimulation of the brain. These compounds appear to act chiefly on the heat-regulating centres, and secondarily by influencing the calibre of the skin-vessels.

W. D. H.

The Action of Electrolytes on Paramœcium. (Miss) DOROTHY DALE (*J. Physiol.*, 1913, **46**, 130—140).—Experiments were performed to determine the C_H limits fatal to Paramœcium. These for a

given "buffer" are constant for the various cultures used, and are different for different "buffers." The simple tervalent positive ions are more potent than the complex tervalent ions. The action of the former, although similar to that of increased C_H, is not explained by hydrolytic dissociation. The action of various ions on the changes of movement is described. The action of hydrogen and hydroxyl ions and of multivalent cations and anions may possibly be ascribed to the power they possess of conferring electric charges on colloidal materials. W. D. H.

The Mechanism of Histamine Action. C. OEHME (*Arch. expt. Path. Pharm.*, 1913, **72**, 76—96).—Histamine (4 β iminoethylglyoxaline) is a base which Barger and Dale separated from the intestinal mucous membrane (A., 1911, ii, 217), and is also formed by bacterial action from the intestinal contents (Mellanby and Twort, A., 1912, ii, 853). In minute doses it is fatal to rabbits, producing a great fall of blood pressure, and the other symptoms of anaphylactic shock. The lethal dose is larger if the injection is made into the mesenteric vein instead of into the systemic circulation; it is therefore possible that the liver may have some action in destroying the poison. Slow injection into the jugular vein also lessens its toxicity, and the question is discussed whether this is due to its being destroyed in the blood, or to its removal from the blood. No evidence of actual destruction in the blood itself was discovered, and only traces pass into the urine. When tested on the isolated uterus, the same difference as to whether the injection or addition to Locke's fluid is made rapidly or slowly is noticeable, as in the intact animal. The uterine tissues take up the drug, and this can subsequently be washed out. The question of its activity seems to be related mainly to the concentration. W. D. H.

The Urinary Elimination of Morphine Injected into an Unaccustomed Animal. H. DOBLENCOURT (*Compt. rend.*, 1913, **156**, 1338—1340. Compare Totze, A., 1904, ii, 220; Bettink, A., 1905, ii, 546).—In the case of the rabbit the intramuscular injection of morphine hydrochloride to the extent of 0·15 gram per kilo. of body-weight is always followed by urinary elimination of the alkaloid as such. This elimination begins within an hour of injection, is at its maximum from the second to the fourteenth hour, and ends after seventy-two hours. The total elimination amounts to about 4% of the alkaloid injected, and only traces of dioxymorphine could be detected in the urine. The animals employed had never previously had morphine, and received only one injection. W. G.

Influence of Some Derivatives of Quinoline and of Naphthaquinoline on the Elimination of Uric Acid. RICCARDO CIUSA and RICCARDO LUZZATTO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 305—311).—2-p-Methoxyphenylquinoline-4-carboxylic acid, $C_{17}H_{13}O_3N$, forms yellow scales, m. p. 217°. 2-p-Dimethylamino-

phenylquinoline-4-carboxylic acid, $C_{18}H_{16}O_2N_2$, forms ruby-red crystals, m. p. 192° (decomp.). 6-Amino-2-phenylquinoline-4-carboxylic acid, $C_{16}H_{12}O_2N_2$, has m. p. 160° (decomp.). 2-Phenyl-β-naphthaquinoline-4-carboxylic acid gives a *methyl* ester, m. p. 124°. In the preparation of the acid, a *dihydro*-derivative, $C_{20}H_{15}O_2N$, is also formed; it has m. p. 226°. A yellow *substance* of acid properties and m. p. 275° also occurs in the preparation of 2-*p*-dimethylaminophenyl-β-naphthaquinoline-4-carboxylic acid.

The authors have investigated the influence of these acids and of a number of others on the excretion of uric acid (compare Nicolaier and Dorn, *Arch. klin. Med.*, 1908, **93**, 331). There is no increase of uric acid after administration of 2-*p*-methoxyphenylquinoline-4-carboxylic acid, 2-*p*-dimethylaminophenylquinoline-4-carboxylic acid or 6-amino-2-phenylquinoline-4-carboxylic acid. A small increase (15—18%) occurs with 2-*o*-hydroxyphenyl-β-naphthaquinoline-4-carboxylic acid. A greater increase (18—27%) is observed with 2-*p*-dimethylaminophenyl-β-naphthaquinoline-4-carboxylic acid, 2-phenyldihydro-β-naphthaquinoline-4-carboxylic acid, and with 2-phenyl-β-naphthaquinoline. Great increases occur after administration of 2-phenylquinoline-4-carboxylic acid ("atophan") and 2-phenyl-β-naphthaquinoline-4-carboxylic acid ("diapurine"). The increase is somewhat less with the latter substance, but it is better tolerated.   R. V. S.

Poisoning by Acid. GERTRUDE D. BOSTOCK (*Zeitsch. physiol. Chem*, 1913, **84**, 468—477).—Subcutaneous injection of glycine in rabbits has no protective action against the fatal effect of acids given by the stomach. The simultaneous administration of ammonium acetate with the acid hastens death. In acid poisoning, the ammonia in the urine increases absolutely and relatively; there is also a rise in total urinary nitrogen. The increase in the ammonia is much greater if glycine or ammonium acetate is given at the same time.   W. D. H.

Distribution of Ante-mortem Administered Arsenic in the Human Cadaver. JOHN B. EKELEY (*J. Amer. Chem. Soc.*, 1913, **35**, 483—485).—The analysis of the corpse of a person who had died from arsenical poisoning showed the presence of the following percentages of arsenic (calculated as As_2O_3) in the various parts of the body: Kidneys, 0·02466; stomach walls, 0·02273; liver, 0·00961; intestines, 0·00377; heart, 0·00125; thigh, 0·00039; toes, 0·00031; brain, 0·00012; spinal cord, a trace.   E. G.

The Influence of the Intestinal Poisons (*p*-Cresol and Indole) on the Central Nervous System of Animals. S. WLADYCZKO (*Ann. Inst. Pasteur*, 1913, **27**, 336—340)—Continued ingestion of small quantities of *p*-cresol and indole, which are formed by the action of putrefactive bacteria on protein degradation products in the intestine, have no visible action on the general health of the animal, as compared with control animals, as a result of the regressive changes in the blood-vessels of the brain. These

alterations, which are produced by the substances, are less marked in the case of guinea-pigs than of rabbits. They have also been observed in an experiment on *Macacus cynomolgus*. Small doses of *p*-cresol and indole also produce after repeated ingestion a slight destructive change in the cellular elements of the central nervous system. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Tyrosinase from Two Enzymes. MARTINUS W. BEYERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 932—937).—By the symbiotic action of *Actinomyces* with a common soil bacterium, tyrosine in an agar plate culture is oxidised to melanin, which appears as black spots on the culture plate. Neither organism alone oxidised tyrosine to the same stage. Other species of *Actinomyces* produce blue, red, or yellow pigments, the simultaneous presence of certain varieties of hay bacteria being favourable in the case of blue and red. Dextrose, malates, and nitrates form the chromogeneous food in this case instead of tyrosine. It is considered that the *Actinomyces* produce homogentisic acid from tyrosine, and that the bacterium oxidises this acid to melanin. Plant tyrosinase (from *Euphorbia lathyis*) is a mixture of these two oxidising enzymes. E. F. A.

The Formation of Lactic Acid by Acetic Acid Bacteria. ALFONS OSTERWALDER (*Centr. Bakt. Par.*, 1913, ii, **37**, 353—364).— When inoculated into sterilised red or white wine, two acetic acid bacteria were found to bring about an increase in the amount of lactic acid. This change was observed in both fresh and fermented wines, and was not affected by the addition of sucrose, lævulose, and malic and tartaric acids. The addition of alcohol was followed by an increase in the amount of lactic acid as well as of acetic acid. Malic acid was decomposed by the organisms, while a reduction in the amount of sucrose was accompanied by an increase in total acids, possibly by the formation of gluconic acid. The fermentation is probably without practical significance, since wines possessing a high acetic acid content are regarded as worthless, and those with little acetic acid would only contain traces of lactic acid as a result of fermentation by these organisms. H. B. H.

Natural Variation of B. acidi lactici with Respect to the Production of Gas from Carbohydrates. J. A. ARKWRIGHT (*J. Hygiene*, 1913, **13**, 68—86).—A bacillus of the *B acidi lactici* group isolated from urine occurred in two varieties, one of which formed gas from sugars and alcohols, and the other of which formed acid, but no gas. Their other characters (serum reactions, etc.) were identical. W. D. H.

Biochemical Activity of Bacillus lactis erythrogenes. MARY LOUISE FOSTER (*J. Amer. Chem. Soc*, 1913, **35**, 597—600).—An investigation of the action of *Bacillus lactis erythrogenes* on milk has shown that it is progressively catabolic, the proteins being ultimately converted into mono- and di-amino-acids. This proteolytic change is probably due to an enzyme. By precipitation with alcohol, a soluble ferment can be obtained, which decomposes the lactose with formation of formic and acetic acids, and this seems to indicate the presence of an intracellular enzyme, which is set free by the alcohol after it has destroyed the organism. These changes in the milk are accompanied by the production of a pigment, which causes a red to dull brown coloration, and can be extracted with amyl alcohol; it is extracellular, since its formation is dependent on the life of the organism.   E. G.

The Inhibitory Selective Action on Bacteria of Substances Related to Monochloroacetic Acid. WILLIAM J. PENFOLD (*J. Hygiene*, 1913, **13**, 35—48).—*B. coli* (Escherlich) when grown on agar to which phenylacetic acid has been added, produces colonies which vary in size, but produce about the same amount of gas from dextrose. When the agar contains monochlorohydrin or sodium monochloroacetate, it throws off variants which ferment alcohol with gas formation, and sugars without gas formation. *B. lactis aërogenes* on monochlorohydrin agar gives rise to variants unable to ferment glycerol. In cases of inhibitory bacterial selection by chemical agents, a comparison of the surviving cells with the original strain indicates what portion or function of the cell is implicated in the cell's intoxication. The cellular enzymes, by virtue of their specific chemical affinities, may play a part in cell intoxication. Phenol, for instance, is rendered more germicidal by the addition of acids; in many media, the cell enzymes produce acids; hence it is probable that phenol selections of bacteria commonly result in the development of new strains with impaired fermenting powers.   W. D. H.

Alcoholic Fermentation. ALEXANDER VON LEBEDEV (*Zeitsch. physiol. Chem.*, 1913, **84**, 308).—Polemical (compare Kostytschev, this vol., i, 323).   E. F. A.

Influence of Respiratory Chromogens on Alcoholic Fermentation. VLADIMIR I. PALLADIN and S. D. LVOV (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 241—252. Compare this vol., i, 430).—The authors have made experiments to ascertain the cause of the influence exerted on the action of zymase by the oxidising processes due to respiratory chromogens. The yeast employed was treated by von Lebedev's method (A., 1911, i, 248), and the chromogens were obtained from turnips, sugar-beets, or mushrooms.

The fermentation of expressed plant juices by killed yeast in a current of air is accompanied by oxidation of the respiratory chromogen of the juice to a pigment, which greatly retards the action of the zymase; the retardation is especially marked when

the juice is oxidised prior to introduction of the yeast. In the case of boiled juice, which is incapable of converting the prochromogen into chromogen and of oxidising the latter to pigment, alcoholic fermentation proceeds readily. Further, no retardation occurs when the unboiled juice is fermented in a stream of hydrogen, which prevents oxidation of the chromogen to pigment.

In cases where the fermentation is delayed, the proportions of alcohol and of carbon dioxide formed are affected to equal extents.

Consideration of these results and of modern views concerning the mechanism of fermentation renders it probable that, in the above experiments, the pigment withdraws the hydrogen liberated in the formation of the intermediate fermentation products and oxidises it, by means of atmospheric oxygen, to water. The absence of the hydrogen necessary for the subsequent synthesis of the alcohol renders the formation of the latter impossible.   T. H. P.

The Use of Ammoniacal Salts in Wine-making. RENÉ MARCILLE (*Compt. rend.*, 1913, **156**, 1336—1338).—An examination of some musts, which took several weeks instead of four or five days for complete fermentation, showed them to be deficient in ammoniacal nitrogen. On the addition of ammonium phosphate to the grape-juice, fermentation proceeded·at the normal rate. Ammonium sulphate gives slightly better results than the phosphate, but care must be taken with respect to plastering. The wine obtained by the slow fermentation was normal in every respect.
                                                                    W. G.

The Action of Cyclamine on Alcoholic Fermentation. JOHAN LUNDBERG (*Arkiv. Kem. Min. Geol.*, 1913, **4**, No. 32, 1—24).—The rate of fermentation at 30° of a sugar solution by means of yeast in the presence of cyclamine was followed by measuring the volume of carbon dioxide evolved (compare Slator, T., 1906, **89**, 128).

Preliminary treatment of the living yeast with a pure solution of cyclamine has no effect on its power of fermentation; in the presence of sugar, however, the activity of the yeast is greatly diminished by the cyclamine. The action of the poison (cyclamine) thus depends on the physiological condition of the cell.

The amount of cyclamine necessary to poison the yeast is proportional to the quantity of the latter. Above a certain limit of concentration of cyclamine a further increase in quantity does not increase the velocity of poisoning.

It is probable that the poisoning is not a simple chemical reaction, but depends on the individual resistance of the cells.

The action of cyclamine on dry yeast depends only on the active yeast present, and not on the total quantity of dry material.

Even in very small concentrations cyclamine has no stimulating action on the yeast fermentation.   T. S. P.

A Ferment of Bitter Wines. E. VOISENET (*Compt. rend.*, 1913, **156**, 1181—1182. Compare A., 1911, ii, 915, 1127).—The ferment from a bitter wine develops in sterile or natural wines, or in wines partly deprived of their alcohol. Thus grown it presents all the

morphological characters of the ferment from the bitter wine. The author names it *Bacillus amaracrylus*. It attacks glycerol, giving acraldehyde, and other products of the fermentation are carbon dioxide, hydrogen, ethyl alcohol, volatile acids, and lactic and succinic acids. It rapidly attacks mannitol and the sugars, acts moderately on dextrin, but does not ferment erythritol, dulcitol, or starch. The fermentation of the sugars, sucrose, lactose, maltose, dextrose, lævulose, and galactose is complete in the presence of calcium carbonate. W. G.

Does the Ferment Causing Bitterness in Wine Consume Cream of Tartar? E. VOISENET (*Compt. rend.*, 1913, **156**, 1410—1412. Compare preceding abstract).—A determination of the tartaric acid in wine before and after it has become bitter shows no difference in the content. Further, if the *B. amaracrylus* is sown on different nutrient solutions containing cream of tartar, no difference can be detected in the tartaric acid content after three months' action. W. G.

Zymase and Reductase in their Mutual Relations. SERGEI LVOV (*Ber. Deut. bot. Ges.*, 1913, **31**, 141—147).—The first or one of the first stages in the alcoholic fermentation of dextrose is the withdrawal of two hydrogen atoms from the dextrose molecule. The hydrogen temporarily attached to the reductase is necessary for the normal course of fermentation.

An exact parallelism exists between the reducing and the fermentative energy of yeast; so that the reducing energy of yeast can be measured by its fermentative energy. The question arises whether reductase exists as a separate, individualised ferment, or whether the reducing properties do not more probably belong to a single, if complicated, fermenting apparatus usually termed zymase? N. H. J. M.

Sugar-free Fermentations of Stereoisomerides. PAUL MAYER (*Biochem. Zeitsch.*, 1913, **50**, 283—287)—Hydroxyfumaric acid, like the corresponding hydroxymaleic acid, undergoes fermentation with yeast, yielding carbon dioxide and acetaldehyde, which was isolated in the form of the *p*-nitrophenylhydrazone. S. B. S.

Replacement of Zinc by Uranium in the Culture of Aspergillus niger. CHARLES LEPIERRE (*Compt. rend.*, 1913, **156**, 1179—1181.* Compare this vol., i, 326, 327).—Uranium, like cadmium and glucinum, can replace zinc in the medium for the culture of *Aspergillus niger*. The weight of crop is normal if the amount of uranium in the form of nitrate is less than 1 in 5000; there is, however, a considerable retardation in attaining the maximum. Sporulation takes place if the amount of uranium is less than 1 in 10,000, but is checked by 1 in 5000. The addition of uranium to media containing zinc produces a marked retardation in growth, but the crop finally attains its normal maximum weight. The uranium is in all cases fixed by the plant. W. G.

* and *Bull. Soc. chim*, 1913, [iv], **13**, 491—498.

Tannic Acid Fermentation. I. Lewis Knudson (*J. Biol. Chem.*, 1913, **14**, 159—184).—Tannic acid is toxic to many fungi in low concentrations. *Aspergillus niger* is a more vigorous fermentative organism than *Penicillium*. Fermentation is more rapid in the gall-nut infusion than in a synthetic solution, in which tannic acid was the only source of carbon. Certain organic compounds in the infusion protect the gallic acid to some extent. The addition of 5% of sugar did not protect the gallic acid, but simply increased the growth; 10% protected the gallic acid entirely. Fermentation can take place under anaerobic conditions, and 1 mg. of mycelium can effect the transformation of 2·7 grams of tannic acid in ten days. The presence of 10% of sugar does not inhibit the secretion of tannase by *Aspergillus niger*, but it does do so to some extent in *Penicillium*. This enzyme is secreted into the culture solution by submersed mycelium as well as by surface growth. There is no evidence that tannic acid is used directly; it is first transformed into gallic acid.   W. D. H.

Tannic Acid Fermentation. II. Effect of Nutrition on the Production of Tannase. Lewis Knudson (*J. Biol. Chem.*, 1913, **14**, 185—202).—There is a progressive increase of tannase in *Aspergillus* and *Penicillium* with increased concentration of tannic acid in Czapek's solution containing 10% sugar. In a full nutrient solution containing 2% tannic acid as a source of carbon, the addition of sucrose decreases the secretion of tannase. *Aspergillus* secretes more tannase (or more active tannase) per unit weight than *Penicillium*. The production of the enzyme is stimulated in both moulds by gallic and especially by tannic acids.   W. D. H.

The Catalytic Action of Light on the Germination of Seeds. Ernst Lehmann (*Biochem. Zeitsch.*, 1913, **50**, 388—392).—Experiments carried out with the seeds of *Epilobium hirsutum* show that in water and in the dark they only germinate very slightly, whereas under otherwise the same conditions 98—100% germinate when exposed to light. The same effect as that produced by light can also be attained by treatment in the dark with solutions of proteoclastic ferments, such as papayotin and trypsin, and by low concentrations of acids (0·05*N*-hydrochloric acid). It appears, therefore, as if light acts catalytically in "mobilising" the proteins of the seeds.   S. B. S.

Influence of Cancer Extracts on the Growth of Lupine Seedlings. Jacob Rosenbloom (*Biochem. Bull.*, 1913, **2**, 229—232). —The extracts had no deleterious effects; but, on the contrary, growth was accelerated; this may be due to inorganic salts.
                                                        W. D. H.

The Action of Poisonous Substances in Different Concentrations on Seeds. The Biochemical Action of Very Concentrated Solutions. V. Arcichovski (*Biochem. Zeitsch.*, 1913, **50**, 233—244).—The action of the following substances was investi-

gated: formalin, sulphuric acid, and silver nitrate. The seeds were soaked in varying concentrations in water of these substances for varying periods, then washed, and allowed to germinate under sterile conditions. The apparatus for carrying out these various operations is described and figured in the text. The number of seeds (pea-seeds) which germinate, and the percentages which start germinating in given times, were ascertained. The toxicity of these substances increases as the concentration is increased up to a certain optimal point. Further increase in the concentration beyond this point diminishes the toxicity. The causes of this phenomenon are discussed by the author.   S. B. S.

Anaerobic Respiration of Various Seed Plants. S. Kos-TYTSCHEV (*Ber. deut. bot. Ges.*, 1913, **31**, 125—129).—Experiments on the amounts of carbon dioxide produced by different plants during anaerobic respiration are described. The ratio $CO_2/EtOH$ varied from $100/100$ to $100/0$.

It seems to be typical of leaves that about half the carbon dioxide is produced by zymase fermentation. Potato tubers produced only traces of alcohol, if any at all, and thus resemble mushrooms, which, however, contain no carbohydrates.

The results obtained support the view that, in most cases, anærobic respiration is not identical with zymase fermentation. As a rule, zymase fermentation takes place at the same time.

N. H. J. M.

The Evolution of Mineral Substances and Nitrogen in Some Annual Plants. GUSTAVE ANDRÉ (*Compt. rend.*, 1913, **156**, 1164—1167. Compare this vol., i, 233).—An extension of the above study to the case of the common flux, spurrey, and *Camelina sativa* shows that, for these three examples of different families of plants, all the mineral elements, as well as the total nitrogen, steadily increase in weight to the time of complete maturity.   W. G.

Experiments with Sterile Cultures of Higher Plants. IVAN SCHULOV (*Ber. Deut. bot. Ges.*, 1913, **31**, 97—121).—The phosphoric acid of lecithin is not assimilated by maize and peas. Phytin is utilised by peas as source of phosphoric acid.

The roots of maize and peas excrete considerable amounts of reducing sugars; maize also excretes malic acid.

Young plants, supplied with ammonium nitrate, take up more ammonia than nitrate; later on the two forms of nitrogen are utilised in about equal amounts, whilst subsequently chiefly nitric nitrogen is taken up by the plant. The physiologically acid reaction initially produced is undoubtedly of importance in the assimilation of phosphates insoluble in water.

The employment of ammonium nitrate causes an increased secretion of organic acids by the roots, and a greater secretion of sugars.   N. H. J. M.

Dry Heating. CARL THOMAE (*J. pr. Chem.*, 1913, [ii], **87**, 423—424. Compare A., 1911, ii, 920; this vol., i, 326, 327).—A

further note on the isolation of the fatty and waxy constituents from plant and animal matters by dry distillation, preferably under diminished pressure. Leaves, pine-needles, blossoms, hay, straw, hair, egg-skins, feathers, wood, and articles manufactured from them, such as cloth, paper, linen, leather, cigars, and wadding, all yield a fat or wax on distillation.

Filter paper and linen gave a white, crystalline wax.   F. B.

Localisation of Betaine in Plants. VLADIMIR STANĚK (*Zeitsch. Zuckerind. Bohm.*, 1913, **37**, 385—390).—The greatest amount of betaine was found in the leaves, especially in young leaves. Leaves of *Amarantus* contained 2·18, and the roots only 0·48% of betaine. The dry matter of sugar beet-roots contained 0·95 to 1·20%, whilst the leaves contained 2·62%. Beet seeds, without husks, contain only traces of betaine; in seeds of *Chenopodium fœtid.*, no betaine was found.   N. H. J. M.

Chemistry of the Floral Pigments. P. Q. KEEGAN (*Chem. News*, 1913, **107**, 181—182).—The colour of blue flowers (gentian, campanula, centaurea, etc.) is attributed to the presence of caffetannin, the only known tannin, except gallotannin, which yields blue oxidation compounds with bases, since it is related to styrene and cinnamic acid. It is doubted whether the presence of an inorganic base is necessary for the production of a blue colour. N. H. J. M.

Chemical Examination of Dicoma anomala. FRANK TUTIN and WILLIAM J. S. NAUNTON (*Pharm. J.*, 1913, [iv], **36**, 694—696).— The material employed for this investigation consisted of the entire air-dried plant of *Decoma anomala*, Sond., which had been specially collected in South Africa.

An alcoholic extract of the plant, when distilled in a current of steam, yielded a small amount of an essential oil, b. p. 130—200°/ ordinary pressure. The portion of the extract which was soluble in water yielded a small amount of a colourless, crystalline *glucoside*, m. p. 243°, which appeared to possess the formula $C_{30}H_{78}O_{17}$, and a large quantity of a yellow, amorphous, deliquescent product, which, when hydrolysed with alkali, gave 3:4-dihydroxycinnamic acid. The aqueous liquid contained, in addition, a quantity of sugar which yielded *d*-phenylglucosazone, m. p. 218°.

The portion of the extract which was insoluble in water formed a dark-coloured, resinous mass. It consisted largely of amorphous products, some of which gave 3:4-dihydroxycinnamic acid on hydrolysis, and a small amount of an amorphous alkaloid was also present. The following definite substances were, however, obtained from the resin: (1) hentriacontane, $C_{31}H_{64}$, m. p. 68°; (2) a *phytosterol*, $C_{28}H_{46}O$, m. p. 159° (*acetyl* derivative, m. p. 133°), which seems to be a lower homologue of stigmasterol; (3) possibly myricyl alcohol; (4) phytosterolin; (5) palmitic, stearic, arachidic, cerotic, and melissic acids, together with some unsaturated acids, which appeared to consist chiefly of a compound, $C_{16}H_{30}O_2$.   H. W.

Occurrence of Gentiopicrin and Gentianose in the Fresh Roots of Gentiana cruciata, L. MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], **7**, 392—395).—Gentiopicrin and gentianose have been isolated in a crystalline condition from the roots of this species (compare A., 1913, i, 149, 434).   T. A. H.

Development of Fat in the Black Walnut (Juglans nigra). II. FRANK M. McCLENAHAN (*J. Amer. Chem. Soc.*, 1913, **35**, 485—493).—In continuation of the work on this subject (A., 1909, ii, 924), analyses have been made of the ovule of the black walnut at various stages of its development. The fat accumulates rapidly up to a certain point, and afterwards increases but slowly. During the early period of development, the fat is waxy in character, but subsequently becomes liquid. In the very young ovule, phosphatides are greatly in excess of fat, but later their relative importance becomes insignificant. The young ovule contains a large proportion of potassium, but this decreases as the fruit approaches maturity. High percentages of calcium, magnesium, and phosphorus are also present during the early life of the ovule, but are relatively unimportant in the later stages.   E. G.

The Anti-toxic Rôle of Calcium with Respect to Some Nutritive Salts in the Culture in Liquid Medium of Peas and Lupins. (Mlle.) C. ROBERT (*Compt. rend.*, 1913, **156**, 915—918). —A comparison of the growth of seedlings of peas and lupins grown on: (*a*) distilled water, (*b*) solutions containing 500 mg. of calcium sulphate per litre, (*c*) solutions containing one of the usual nutrient salts in corresponding strength, (*d*) solutions, being a combination of (*b*) and (*c*). The results show that, with the strength used, calcium is not toxic, but very considerably favours the development of the young plants. The salts of magnesium, potassium, and ammonium are toxic at the concentration used, but the addition of a calcium salt suppresses this toxicity. The development in mixtures of salts of potassium, magnesium, or ammonium with the calcium salt is the same as when the calcium salt alone is used; thus, in the early days of its growth, the salts of those three metals do not seem to act as nutrients to the plant. The white lupin is more sensitive to the toxic action than the pea, very small quantities of potassium salts sufficing to arrest all development.   W. G.

Nutritive Value of Maize Proteins. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxxi—xxxii; *J. Biol. Chem*, **14**).—About one-third of the proteins in maize consists of glutelin, which yields all the amino-acids found in most proteins. Zein causes rapid decline in weight, but may be made of greater value by adding tryptophan or other proteins. Gliadin suffices for maintenance, but not for growth. Glutelin is adequate for growth also.   W. D. H.

Cotton-seed Meal Intoxication. I. Pyrophosphoric Acid. WILLIAM A. WITHERS and BURTON J. RAY (*J. Biol. Chem.*, 1913, **14**, 53—58).—The results indicate that pyrophosphoric acid is not the cause of the toxicity of cotton-seed meal.   W. D. H.

Accumulation of Nitrogen in the Soil by means of Micro-organisms. JOSEF DVOŘÁK (*Zeitsch. landw. Vers. Wesen. Oesterr.* 1912, **15**, 1077—1121).—A detailed account of numerous experiments based on the observations of Stoklasa (A., 1911, ii, 429) and others on the assimilation of nitrogen (atmospheric or otherwise) by plants, and the micro-organisms of the soil.

The influence of various organic substances is studied, and the conclusions arrived at that the ammonium ion is as readily absorbed as the nitrate ion, and that acid soils exhibit the least, and those with a neutral or alkaline reaction the highest, biological absorption.

F. M. G. M.

Fixation of Nitrogen by So-called Zeolites. GEORG WIEGNER (*J. Landw.*, 1913, **61**, 11—56).—Experiments were made to ascertain whether the ammonium fixed by zeolites in soils, or any portion of the ammonia, is rendered unavailable to plants. With regard to the amount of ammonia fixed by 100 grams of permutite it is shown that this varies according to the concentration of the ammonia in the solution.

Pot experiments are described in which oats followed by buck-wheat were manured with ammonium sulphate, without and with calcium zeolite in different amounts, and with ammonium zeolite both without and with calcium zeolite.

The results showed that addition of calcium zeolite increased the dry produce, and did not diminish the nitrogen. With large amounts of nitrogen applied as manure, the nitrogen was better utilised in presence of zeolites, possibly owing to losses in the pots without zeolites.

There can be no question of the permanent fixation of a definite and constant amount of ammonia by zeolites, as the amount which is fixed depends on the concentrations, which are variable. The changes are sometimes favourable and sometimes unfavourable to the plants.   N. H. J. M.

Action of Histidine and Arginine in Soils. J. J. SKINNER (*Bied. Zentr.*, 1913, **42**, 213—214; from *Proc. 8th Internat. Cong. Appl. Chem.*, 1912).—Histidine and arginine, which are produced in soils as primary cleavage products of proteins, are favourable to the growth of plants except when large amounts of nitrates are present, when they have no appreciable effect. Like creatine and creatinine, both substances can take the place of nitrates.   N. H. J. M.

Influence of Sodium Carbonate and the Imperviousness of the Soil on the Growth of Plants. JOHN W. LEATHES (*Bied. Zentr.*, 1913, **42**, 213; from *Proc. 8th Internat. Cong. Appl. Chem.*, 1912).—The result of pot experiments in which alkali soils received

calcium sulphate in amounts sufficient to reduce the sodium carbonate from 0·06 to 0·01% failed to show any appreciable change in the physical properties of the soil. When the sodium carbonate was partly neutralised with calcium sulphate, 33% of the seeds germinated, the best results being obtained with rice and wheat. When the imperviousness of the soil was removed by addition of sodium chloride, 16% of the seeds germinated, but the plants did not ripen.

N. H. J. M.

The Effect of Ignition on the Solubility of Soil Phosphates. CHARLES B. LIPMAN (*J. Ind. Eng. Chem.*, 1912, **4**, 663).—An account of the analysis of five typical soils, as a result of which the author draws the conclusion that the observation of Fraps (A., 1912, ii, 85), that ignition increases the solubility of the phosphates in minerals, does not apply to soils where ignition appears to definitely decrease the solubility of the phosphates; and it is suggested that the increased solubility noted in minerals may be due to mechanical changes induced by heat, which, in disintegrating the particles, increase the amount of surface available for attack by acids.

F. M. G. M.

Zinc as Catalytic Manure. MAURICE JAVILLIER (*Bied. Zentr.*, 1913, **42**, 215; from *Proc. 8th Internat. Congr. Appl. Chem*, 1912).— Field experiments in which oats, maize, rye, clover, and peas received from 1 to 10 kilos. of crystallised zinc sulphate per hectare. The best results were obtained with maize, which always showed increased production under the influence of zinc sulphate, whilst the other plants gave irregular results.

Laboratory experiments were made with *Aspergillus niger*, showing the effect of zinc on the assimilation of carbohydrates, nitrogen, and minerals, and on the composition of the plant. N. H. J. M.

Aluminium Sulphate as Catalytic Manure. GABRIEL BERTRAND and HENRI AGULHON (*Bied. Zentr.*, 1913, **42**, 215; from *Proc. 8th Internat. Congr. Appl. Chem.*, 1912)—Small amounts of aluminium sulphate (2 mg. per kilo. of soil) increased the yield of barley 18%, or 17% calculated on the dry matter. With 4 mg., the dry produce was not increased, whilst there was a gain in the fresh produce.

N. H. J. M.

Employment of Manganese as Catalytic Manure. GABRIEL BERTRAND (*Bied. Zentr.*, 1913, **42**, 214; from *Proc. 8th Internat. Cong. Appl. Chem.*, 1912).—In pot experiments with peas and barley it was found that addition of manganese sulphate increased the yield by 10—20%. Field experiments gave similar results, oats being increased 9·5% by 60 kilos. of manganese sulphate per acre, peas 20% by 30 kilos., colza 18%, and clover 15% by 40 kilos. of manganese sulphate. The most suitable amounts of manganese sulphate are 30 to 50 kilos. of the anhydrous salt per hectare. N. H. J. M.

Organic Chemistry.

Magnesium in Organic Chemistry. VICTOR GRIGNARD (*Bull. Soc. chim*, 1913, [iv], **13**, i—xxxvii).—An address delivered to the Chemical Society of France on February 13th, 1913. T. A. H.

Synthesis of Methane by Catalysis. VLADIMIR N. IPATIEV (*J. pr. Chem.*, 1913, [ii], **87**, 479—487; *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 433—442).—According to the author the synthesis of methane from its elements in the presence of metals is not a direct combination of the elements, but consists in a catalytic oxidation of the carbon, by means of the metallic oxide contained in the metal, to carbon dioxide, which then undergoes a catalytic reduction to methane, the water formed in the latter reaction being subsequently decomposed by the metal with the regeneration of the metallic oxide.

In support of this view, the author describes a series of experiments showing (1) that methane is formed by heating carbon at $500—520°$ in hydrogen under pressure and in the presence of metallic oxides (nickel, copper, tin, iron); (2) that metallic nickel, containing $98·41\%$ of the metal and not further reducible, brings about the catalytic synthesis of methane from carbon and hydrogen under pressure at $500—510°$, the amount of methane formed being far greater than that corresponding with the carbon dioxide which could be formed from the oxygen in the apparatus or combined with the metal; (3) that methane in the presence of nickel and water is decomposed under pressure at $485—520°$ with the formation of hydrogen and carbon dioxide, and (4) that the latter reaction is reversible, a mixture of carbon dioxide and hydrogen, when heated under pressure in the presence of metallic nickel or copper, or the oxides of these metals, yielding water and methane. F. B.

The Relation between the Crystal-Symmetry of the Simpler Organic Compounds and their Molecular Constitution. I. WALTER WAHL (*Proc. Roy. Soc.*, 1913, *A*, **88**, 354—361).—This paper simply contains the experimental data concerning the aliphatic hydrocarbons; general conclusions will be given later. Methane crystallises in the regular system (compare A., 1912, ii, 1041). The crystallographic systems of other hydrocarbons are as follows: ethane, hexagonal; propane is polymorphic, giving rhombic, prismatic needles which, with rise in temperature, give crystals which are either rhombic or monoclinic; β-methylpropane is possibly rhombic, but the matter is uncertain; $\beta\beta$-dimethylpropane gives cubical crystals, which at low temperature change into crystals which are probably tetragonal; n-butane is hexagonal, changing at a temperature close to that of liquid air to rhombic crystals; n-pentane is rhombic; n-hexane is either monoclinic or triclinic, probably the former; n-heptane and n-octane are either monoclinic or triclinic, it is uncertain which. T. S. P.

Polymerisation of Ethylene at High Temperature and Pressure in the Presence of Catalysts. VLADIMIR N. IPATIEV and O. RUTALA (*Ber.*, 1913, **46**, 1748—1755. Compare A., 1911, i, 937).—In a previous paper (*loc. cit.*), it has been shown that the presence of alumina does not affect the nature of the products formed by the polymerisation of ethylene, but has a marked influence on their relative amounts. The present work was undertaken to test the influence of zinc chloride and aluminium chloride.

Ethylene readily undergoes polymerisation when heated under a pressure of about 70 atmospheres at 275° in the presence of zinc chloride. The residual gas has the composition: C_nH_{2n} 36%, H_2 3%, C_nH_{2n+2} 61%. The liquid products were fractionated, and those boiling below 85% found to consist mainly of pentane and hexane, *iso*pentane being isolated from one of them in an approximately pure state. Methyl*cyclo*butane was not detected. In the fractions of b. p. 50—300°, the proportion of ethylenic hydrocarbons increases regularly with increasing temperature, whilst those boiling below 145° contain only ethylene and saturated hydrocarbons.

The individual fractions were treated with fuming sulphuric acid and the residue again fractionated, all the fractions so obtained being unacted on by nitrating mixture or permanganate. Those boiling below 130° consisted almost entirely of paraffin hydrocarbons; in those of higher b. p. an increasing quantity of polymethylene hydrocarbons was found, so that the fraction b. p. 256—265° contained practically only naphthenes.

The portion of the original product of b. p. above 280° was distilled under diminished pressure. The fractions obtained were uniform in ultimate composition and consisted of a mixture of ethylene hydrocarbons and naphthenes.

Ethylene is scarcely affected by commercial aluminium chloride at 240° and about 70 atmospheres pressure. At 280° it gives a charred residue and a gas having the composition C_nH_{2n} 4·0%, H_2 10·0%, C_nH_{2n+2} 86%. With freshly prepared aluminium chloride at 200°, liquid products were not obtained, and only a charred residue remained in the apparatus; liquid products were, however, prepared at the ordinary temperature. These were fractionated as before, and, after removal of unsaturated hydrocarbons by means of fuming sulphuric acid, again distilled, when the fractions, b. p. below 200°, were found to consist mainly of paraffin hydrocarbons, naphthenes being only present in the portion, b. p. above 200°. The polymerisation of ethylene in the presence of aluminium chloride yields, therefore, considerably less naphthenes than with zinc chloride as catalyst.   H. W.

$\Delta^{\alpha\gamma}$-**Hexatriene.** PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1184—1187. Compare van Romburgh and Dorssen, A., 1906, i, 130, 722).—A specimen of $\Delta^{\alpha\gamma}$-hexatriene which had been preserved for five years was distilled, when fully 50% passed over below 80° (the hydrocarbon has b. p. 78·5—80°/766 mm.). From the residue a *substance*, b. p. 99·5°/16mm., D^{11} 0·880, n_D^{11} 1·51951, was isolated, which appears to be a dimeride of hexatriene. It readily forms an additive *product* with bromine (1 mol.), whilst, on further

addition of the latter reagent, much hydrogen bromide is evolved. It is rapidly oxidised by potassium permanganate.

[With MULLER.]—$\Delta^{\alpha\gamma\epsilon}$-Hexatriene has been regenerated from its crystalline dibromine additive compound (*loc. cit.*). A solid compound has also been obtained from $\Delta^{\alpha\gamma\epsilon}$-hexatriene and sulphur dioxide, investigation of which is incomplete, but from which the hydrocarbon may also be regenerated. The latter has also been prepared by dehydration of $\Delta^{\alpha\epsilon}$-*hexadiene-δ-ol* by the action of potassium hydrogen sulphate or phthalic anhydride.

[With LE HEUX.]—$\Delta^{\alpha\epsilon}$-Hexadiene-δ-ol has been prepared by the action of allyl bromide, zinc turnings, and absolute ether on acraldehyde. It has b. p. 132·2—132·4°/769 mm., $D_4^{10·5}$ 0·8698, $n_D^{10·5}$ 1·45231. With acetic anhydride and a drop of sulphuric acid, it yields the corresponding *acetate*, b. p. 151·2—152·7°. Phosphorus tribromide converts it into the *bromide*, b. p. 59—63°/35 mm., which very readily absorbs bromine (1 mol.); further quantities of bromine react very slowly without yielding, however, hydrogen bromide.

By reduction of the chloroacetin of s-divinyl glycol with a copper-zinc couple in ethereal solution with addition of hydrochloric acid, a liquid, b. p. 77—81°, has been obtained, which, when strongly cooled, becomes crystalline and consists very probably of $\Delta^{\alpha\gamma\epsilon}$-hexatriene. With bromine it gives a dibromide identical with that obtained from the said hydrocarbon. H. W.

Preparation of Chloro-derivatives of the Amyl Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 258555).—When the vapour of β-methyl-Δ^β-butylene and chlorine are allowed to react at the ordinary temperature and under a pressure of about 50 mm., they give rise to tertiary *iso*amyl chloride and other products which can be employed for the preparation of isoprene. F. M. G. M.

Preparation of Dihalogenated Hydrocarbons. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 259192. Compare this vol., i, 583).—Dichloro*iso*hexane (b. p. 155—160°) is obtained when the vapour of tertiary chloro*iso*hexane is treated with chlorine under reduced pressure; dichloro*iso*butane (b. p. 108—109°) is prepared in a similar manner from chloro*iso*butane, whilst if tertiary bromo*iso*butane (b. p. 72°) is employed it furnishes a satisfactory yield of chlorobromo-*iso*butane. F. M. G. M.

Physical Constants of Certain Chlorinated Hydrocarbons Employed as Solvents. II. WALTER HERZ and W. RATHMAN (*Chem. Zeit.*, 1913, 37, 621—622).—The following freezing point and specific heat data are recorded: s-tetrachloroethane $-36°$, 0·268; pentachloroethane $-22°$, 0·266; trichloroethylene $-73°$, 0·223; tetrachloroethylene $-19°$, 0·216. The specific heats refer to 20°.

Commercial dichloroethylene consists of a mixture of the *cis*- and *trans*-forms, which can be separated by fractional distillation. The *cis*-form boils at 48·8°/763 mm.; its density is given by the equation: $D = 1·2908 - 0·00168t$, and its coefficient of expansion is 0·00136. The *trans*-form boils at 59·8°/763 mm.; its density is

given by $D = 1\cdot3144 + 0\cdot001605t$, and its coefficient of expansion is $0\cdot00127$.

The vapour pressures of the two isomerides have also been determined at a series of temperatures. By substitution of the data in Clausius's equation, the latent heat of vaporisation of the *cis*-form is found to be 6930 cal. (43—48·8°), and that of the *trans*-form 7268 cal. (54·8—59·8°).   H. M. D.

Some New Properties of Carbon Tetraiodide and its Estimation in Presence of Iodoform. MARCEL LANTENOIS (*Compt. rend.*, 1913, 156, 1629—1631. Compare this vol., i, 583). —Carbon tetraiodide is attacked by hydrogen at 100°, giving iodoform and hydrogen iodide, and at the same time small amounts of di-iodomethane and methyl iodide are formed. This hydrogenation is readily brought about by alcoholic potassium hydroxide at 30—40°, a small quantity of methane being present in the product. Sodium in liquid ammonia reacts with carbon tetraiodide (3 mols.), giving methane (1 mol.), together with some sodium cyanide, methylamine, and another base, probably guanidine.

Oxygen readily attacks carbon tetraiodide, even in the dark, giving iodine and carbonyl iodide, which is unstable, and yields carbon monoxide with a small proportion of carbon dioxide, the reaction being facilitated by light.

Silver nitrate in aqueous solution (20%) reacts with iodoform, giving carbon monoxide quantitatively. With carbon tetraiodide, it gives both carbon monoxide and carbon dioxide in the proportion of 3 : 1 by volume. One molecule of the tetraiodide gives one molecule of gas, thus giving a means of estimating it alone or in the presence of iodoform.   W. G.

Density and Thermal Expansion of Ethyl Alcohol and its Mixtures with Water. N. S. OSBORNE, E. C. McKELVY, and H. W. BEARCE (*J. Franklin Inst.*, 1913, 175, 165—167. Compare A., 1912, i, 232).—An abstract of, with a short discussion on, a paper by Pulfrich (*Zeit. für Inst. K.*, 13, 456), describing different methods of purifying ethyl alcohol, and the varying physical constants exhibited by different specimens thus obtained with an investigation on the thermal expansion of the same when diluted with varying proportions of water.   F. M. G. M.

Catalytic Hydrogenation of Acetylenic γ-Glycols in the Presence of Palladium-black. GEORGES DUPONT (*Compt. rend.*, 1913, 156, 1623—1625).—The reduction of acetylenic γ-glycols in the presence of platinum-black gives the saturated glycol (formula 1) together with the alcohol (formula II), but never any of the saturated hydrocarbon (formula III) (compare Lespieau, A., 1910, i, 535) :

(I.) $OH\cdot CRR'\cdot[CH_2]_2\cdot CRR'\cdot OH$.   (II.) $OH\cdot CRR'\cdot[CH_2]_2\cdot CHRR'$.
(III.) $CHRR'\cdot[CH_2]_2\cdot CHRR'$.
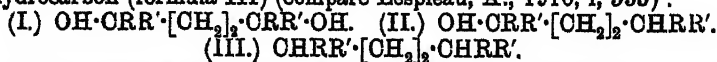
If for the platinum-black is substituted palladium-black, in most cases the product of hydrogenation contains only traces of the

glycol with a little of the alcohol, and large quantities of the hydrocarbon.

In the case of the aliphatic glycols of the type dimethylbutinenediol, the hydrogenation is limited and the result is a mixture of the three possible products. With the aromatic glycols, whilst platinum-black gives only the saturated glycol (formula I), palladium-black gives only the saturated hydrocarbon (formula III); thus diphenyldimethyl-butinenediol gives quantitatively *βε-diphenylhexane*, a colourless liquid, b. p. 185°/12 mm., D^{15} 0·9634, n_D 1·5440. W. G.

Preparation of Mesityl Oxide from Diacetone Alcohol [*iso*-Hexan-δ-ol-β-one]. MORITZ KOHN (*Monatsh.*, 1913, 34, 779—780).—The conversion of *iso*hexan-δ-ol-β-one,

$$OH·CMe_2·CH_2·COMe,$$
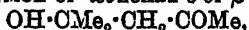
the primary product in the condensation of acetone to mesityl oxide, into mesityl oxide does not require a large quantity of sulphuric acid as previously supposed. When 290 grams of *iso*hexan-δ-ol-β-one to which sixty drops of sulphuric acid have been added are quickly distilled through a fractionating column, the distillate contains about 190 grams of mesityl oxide. D. F. T.

Action of a-Monochlorohydrin and Epichlorohydrin on Monosodium Glyceroxide. JEAN NIVIÈRE (*Compt. rend.*, 1913, 156, 1628—1629).—a-Monochlorohydrin is readily prepared by saturating glycerol at 120—130° with hydrogen chloride, a yield of 66% being obtained. The product reacts with monosodium glyceroxide, glycerol being regenerated and at the same time 2—3% of diglyceryl alcohol is produced. Epichlorohydrin, which is readily obtained (95% yield) by the action of strong aqueous potassium hydroxide on ay-dichlorohydrin under reduced pressure, reacts with monosodium glyceroxide, giving a *polymeride* of the internal anhydride of the diglyceryl alcohol. This is a white, amorphous substance, insoluble in water and the ordinary solvents, and yields a *diacetyl* derivative on boiling with acetic anhydride and anhydrous sodium acetate. Both of these substances decompose without melting. W. G.

Preparation of Diglyceryl Alcohol. JEAN NIVIÈRE (*Compt. rend.*, 1913, 156, 1776—1778. Compare preceding abstract).—In an attempt to prepare diglyceryl alcohol the author has prepared the diacetyl derivative of monochlorohydrin and caused it to react with monosodium glyceroxide, the product being a small quantity of the diacetyl derivative of the required alcohol and a considerable residue analogous to the vegetable mucilages.

By warming the internal anhydride of glycerol with anhydrous glycerol in equimolecular proportions on a water-bath for seven hours and acetylating the crude product with acetic anhydride, the *tetracetyl* derivative of the required alcohol is obtained as an oily liquid, b. p. 196—197°/3 mm., D^{17} 1·1835. On saponification with alcoholic sodium hydroxide it yields *diglyceryl alcohol*, $C_6H_{14}O_5$, a pale yellow, very viscous liquid, b. p. 235—240°/6 mm. W. G.

Efficiency of the Preparation of Ethyl Ether from Alcohol and Sulphuric Acid. Percy N. Evans and Lena M. Sutton (*J. Amer. Chem. Soc.*, 1913, **35**, 794—800).—An account is given of experiments made with a view to determine the efficiency of the reaction between ethyl alcohol and sulphuric acid. It has been found that the degree of completeness of the reaction $2Et \cdot OH = Et_2O + H_2O$ amounts to about 40%. This efficiency was maintained in some experiments until the distillate amounted to as much as one hundred and seventy-six times the original volume of the sulphuric acid, or until the ether produced was forty times the volume, or sixteen times the weight, of the acid used. The efficiency decreased abruptly when there remained in the flask a charred, semi-solid residue of about one-twentieth of the weight of the acid originally present. The decrease in efficiency is not due to accumulation of water, as the reaction proceeds normally with dilute sulphuric acid. From 15—20% of the sulphuric acid is lost as sulphur dioxide.   E. G.

Crystalline Glycerophosphates. Rogier and Fiore (*Chem. Zentr.*, 1913, i, 1330—1332; from *Bull. Sci. Pharmacol.*, 1913, **20**, 7—25, 72—86).—Technical sodium glycerophosphate,
$$Na_2PO_3 \cdot O \cdot C_3H_7O_2,$$
usually forms small needles with $5H_2O$, but sometimes large tablets with $6H_2O$. The concentrated solution at 18° contains 27·38% anhydrous salt, and may be heated to 120° without decomposition. Cryoscopic methods gave one-third of the calculated molecular weight, so a physiological serum should only contain 35 grams. The following salts have been made by double decomposition. *Calcium* salt, $CaPO_3 \cdot O \cdot C_3H_7O_2$, microcrystalline or large crystals by slow evaporation, solubilities, 1% at 0°, 1·63% at 18°, 0·43% at 60°; *barium* salt, with $1H_2O$ which is lost on boiling the solution, solubility 4·50% at 21°; *strontium* salt, leaflets with $2H_2O$, solubility 2·09% at 19°, 0 80% at 60°; *quinine* salt, $B_2PO_3 \cdot O \cdot C_3H_7O_2 + 4H_2O$, white needles, m. p. 180—181°, $[\alpha]_D^{21} - 133°33'$, $[\alpha]_D^{17} - 140°24'$; *acid strychnine* salt, $BPO_3H \cdot O \cdot C_3H_7O_2, H_2O$, m. p. 260°, $[\alpha]_D^{23} - 25°40'$; *brucine* salt, $B_2PO_3 \cdot O \cdot C_3H_7O_2, 11H_2O$, prisms, m. p. 192°, $[\alpha]_D^{13} - 29°35'$; *basic copper* salt, $Cu[(Cu \cdot OH)PO_3 \cdot O \cdot C_3H_7O_2]_2, 6H_2O$, dark blue powder; *copper* salt, $CuPO_3 \cdot O \cdot C_3H_7O_2, H_2O$, pale blue needles.   J. C. W.
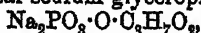
Oxidation of Lecithin in Presence of Iron Salts. Otto Warburg and Otto Meyerhof (*Zeitsch. physiol. Chem.*, 1913, **85**, 412—414).—The mixture of substances known as lecithin is very readily oxidised by atmospheric oxygen in aqueous suspension in presence of iron salts, whereas other important cell constituents are stable under similar conditions. There is a close parallelism between the velocity of lecithin oxidation in vitro and the rate of the oxidation processes in the living cell based on the amount of lecithin present.
                                                                E. F. A.

The Action of Alkali Arsenite on Ethyl Disulphide. August Gutmann (*Ber.*, 1913, **46**, 1474—1475).—Weinland and Rumpf (A., 1897, ii, 257) have shown that sodium disulphide acts on trisodium

arsenite with the formation of trisodium monothioarsenate, Na_3AsO_3S, and sodium sulphide. It was to be expected that ethyl disulphide would act similarly to the sodium disulphide, if it entered into reaction at all, but the author finds that this is not the case, the reaction proceeding readily in the cold with the formation of trisodium arsenate and ethyl mercaptan. This reaction is explained by the author by assigning a peroxide character to the ethyl disulphide, which takes hydrogen from the water, leaving oxygen available for oxidising the arsenite. T. S. P.

Hexadecanesulphonic Acid. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1913, **27**, 110—113. Compare A., 1912, i, 600) —Cetyl iodide reacts with sodium hydrogen sulphide in alcoholic solution to give *cetyl mercaptan*, $C_{16}H_{33}\cdot SH$, which is precipitated as a yellow solid on the addition of water, and on warming this with potassium permanganate solution it is oxidised to the sulphonic acid. The manganese dioxide is filtered off, the solution neutralised with acetic acid, and a slight excess of lead acetate added. The precipitated lead salt is collected, washed, dried, suspended in alcohol, and decomposed by hydrogen sulphide. After filtering and evaporating off the alcohol, *cetylsulphonic* [*hexadecanesulphonic*] *acid*, $C_{16}H_{33}\cdot SO_3H$, is obtained, soluble in alcohol, ether, benzene, and acetic acid, crystallising from the latter in microscopic plates. It behaves like a semi-hard soap, and is a comparatively strong acid, yielding *sodium* and *potassium* salts, which are soluble in water, and closely resemble the alkali palmitates in their behaviour. The *barium* and *lead* salts are insoluble in water. W. G.

The Physico-chemical Properties of Hexadecanesulphonic Acid and Sodium Hexadecanesulphonate. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1913, **27**, 113—128. Compare preceding abstract).—Hexadecanesulphonic acid and its sodium salt in aqueous solution possess the property of emulsifying with toluene, but, unlike the oleates, are only very slightly extracted by that solvent. On the other hand, they possess the property of removing fat from, and cleansing wool in the same manner as, an ordinary soap. The elevation of the boiling point of water on solution either of the acid or its salt does not bear any relation to the concentration of the solutions, and this method gives a wide range of values for the molecular weights. The author has made a complete study of the electrical conductivity of the sodium salt and the free acid at different temperatures and varying concentrations. In the case of the sodium salt, the readings give a sharp indication of the temperature, 38—37°, at which crystallisation takes place. The values obtained for the molecular conductivity in solutions from $0.01665N$ to $0.0666N$ are practically independent of the concentration. The free acid furnishes an excellent example of a colloidal substance, and permits of the direct examination of the molecular problem and of an intermolecular liquid. The values obtained for the molecular conductivity diminish steadily as the dilution passes from 15 to 30 litres, remains constant from 30 to 60 litres, and finally increases regularly and proportionately as the dilution increases. W. G.

The Use of Calcium Carbonate as Catalyst for Organic Acids and their Anhydrides. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1913, **156**, 1730—1734)—Precipitated calcium carbonate can be employed as a catalyst at 450—500° for the conversion of acids into the ketones, but in the acetic acid series the yield diminishes as the molecular weight increases. Whilst acetic acid gives a theoretical yield of propanone, valeric acid only gives a yield of 32% of dibutyl ketone. Despite blackening due to deposition of carbonaceous products, the calcium carbonate retains its activity and can be employed a great number of times, but its use is not so advantageous as that of thorium oxide (compare Senderens, A., 1912, i, 537) for the higher ketones. Benzoic acid mixed with the aliphatic acids yields mixed ketones under the above conditions. The acids can be replaced by their anhydrides in every case, and whilst benzoic acid alone cannot be converted into benzophenone by this method, a certain amount of this ketone can be obtained by the use of benzoic anhydride.

W. G.

Esters Derived from Octanol by the Author's Method; Observations on the Principle of this Method. JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1913, **156**, 1620—1623 ; *Bull. Soc. chim.*, 1913, [iv], **13**, 586—591).—By their method using sulphuric acid (2—3%) as catalyst (compare A., 1911, i, 600, 637 ; ii, 1080 ; 1912, i, 694 ; this vol., i, 42) the authors have prepared the following esters of octanol, of which only the acetate was previously known (compare Bouis, this Journ., 1854, **7**, 280) :

Ester.	B. p./74·4 mm.	D_4^{14}.
Formate	184·0°	0·8642
Acetate	194·5	0·8626
Propionate	211·5	0·8611
Butyrate	227·5	0·8592
*iso*Butyrate	220·0	0·8554
*iso*Valerate	236·5	0·8540

The *phenylacetate*, b. p. 195°/35 mm., D_4^{14} 0·9503, is decomposed on distilling at the ordinary pressure.

The authors claim that their method is entirely distinct from that of Fischer and Speier (A., 1896, i, 201), where a large excess of alcohol is used and stronger acid, which merely acts as a dehydrating agent. The organic acids are capable of division into two classes. The first contains the aromatic acids with the carboxyl group attached to the nucleus, in which case their method is useless. The second class contains the fatty acids and aromatic acids with the carboxyl group in a side-chain, and here their dilute acid acts as a true catalyst and an excess of alcohol is unnecessary. A compound of the type $RH \cdot SO_4$ is first formed, and then a cycle of reactions goes on :

$$R \cdot HSO_4 + R \cdot OH = R_2SO_4 + H_2O$$
$$R_2SO_4 + R'CO_2H = R'CO_2R + RHSO_4.$$
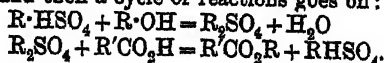
W. G.

Graded Degradation of Different Saturated Mono- and Di-basic Acids. PHILIPPE BARBIER and RENÉ LOCQUIN (*Compt. rend.*, 1913, **156**, 1443—1446).—The transformation of a saturated acid of the

type $R \cdot CH_2 \cdot CO_2H$ into its next lower homologue can be brought about by first converting the acid into the corresponding tertiary alcohol, $R \cdot CH_2 \cdot CMe_2 \cdot OH$, by the action of magnesium methyl iodide, and then submitting this to oxidation :

$$R \cdot CH_2 \cdot CMe_2 \cdot OH + 3O = R \cdot CO_2H + CH_3 \cdot CO \cdot CH_3 + H_2O.$$
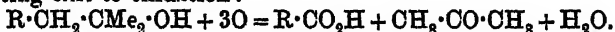
Thus *iso*valeric acid is first converted into $\beta\delta$-dimethylpentan-δ-ol, which on oxidation with chromic acid yields *iso*butyric acid. Decanoic acid is similarly converted into pelargonic acid.

By the interaction of *iso*amyl bromide and ethyl methylmalonate, *aδ-dimethylhexoic acid*, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CO_2H$, b. p. 228—230°/ 760 mm. and 127—130°/18 mm., is obtained, giving a *methyl* ester, b. p. 172—173°, an *acid chloride*, b. p. 69°/16 mm., an *amide*, m. p 99—100°, and a p-*toluidide*, m. p. 75°. With magnesium methyl iodide it yields $\beta\gamma\zeta$-*trimethylheptan-β-ol*, b. p. 92—95°/18 mm., which on oxidation with dilute nitric acid gives a neutral and an acid product. The acid product is a mixture of acetic, *iso*valeric, and *iso*hexoic acids, whilst the neutral product consists principally of methyl *iso*amyl ketone, together with a small quantity of an unsaturated hydrocarbon, b. p. 160—165°. β-Methyladipic acid on treatment with magnesium methyl iodide and subsequent oxidation yields a certain amount of methylsuccinic acid and some diethylenic hydrocarbon.

With the monobasic acids where the $\cdot CO_2H$ group is attached to a $\cdot CH_2$ group, they are simply converted into their next lower homologue. With an a-substituted acid the principal product is a ketone. The dibasic acids behave in the same way as the monobasic acids, the degradation proceeding simultaneously on the two terminal carboxyl groups.   W. G.

Synthesis of the Glycerides of Lauric Acid. B. W. VAN ELDIK THIEME (*Ber.*, 1913, 46, 1653—1657. Compare A., 1912, i, 333). —A reply to Grün (this vol., i, 157), criticising the latter's experimental results. The author re-affirms that even under the modified conditions stated by Grün (*loc. cit.*) the so-called synthesis of a-dilaurin yields a mixture of trilaurin, crystalline dilaurin, liquid dilaurin, and monolaurin.   D. F. T.

Nickel Oxides as Reduction Catalysts in the Addition of Molecular Hydrogen to Unsaturated Fats and Fatty Acids. FRED BEDFORD and ERNST ERDMANN (*J. pr. Chem.*, 1913, [ii], 87, 425—455 ; *J. Russ. Phys. Chem. Soc.*, 1913, 45, 616—643).— Unsaturated fats and fatty acids undergo catalytic reduction at the ordinary pressure in the presence of nickel oxide, the rate of reduction being much greater than when metallic nickel is employed. In addition to its greater activity, the oxide possesses the advantage over the metal in that it is far less sensitive to hydrogen sulphide and other substances which exert a deleterious effect on the activity of the metal. All three oxides of nickel may be used as catalysts, nickelous and nickelic oxides requiring a temperature of 250°, whilst in the presence of the suboxide the reduction proceeds readily at 180—200°.

During the reduction, the higher oxides become converted into the suboxide, which forms a deep black, colloidal solution with the oil or fat.

Nickel suboxide may be distinguished from metallic nickel by its inability to form nickel carbonyl with carbon monoxide, and by its much smaller electric conductivity.

A nickelic oxide, which has already been used in the catalytic reduction, possesses a greater activity than a fresh specimen on account of the presence of suboxide.

The velocity of hydrogenation is increased by employing a voluminous oxide, prepared by gentle ignition of the nitrate, and also by the addition of small quantities of other metallic oxides (Al, Ag, Zr, Ti, Ce, La, Mg).

Nickel salts of organic acids (formic, acetic, oleic, and linolenic) in the presence of unsaturated fats are reduced at 200—250° to the oxide or to metallic nickel, and may therefore be used as catalysts; thus, nickel formate is reduced at 210° to the suboxide and at 250° to metallic nickel. F. B.

Ricinoleic Acid. BERTHOLD RASSOW [with J. RUBINSKY] (*Zeitsch. angew. Chem.*, 1913, **26**, 316—320).—The authors have investigated the action of heat on ricinoleic acid. Since the products formed are amorphous, yield amorphous salts, and have very similar solubilities, their isolation in the pure state has not been accomplished. Their chemical nature is deduced from observations of acid number, saponification number, acetyl number, iodine number, and molecular weight. The following are the main results obtained.

Ricinoleic acid is decomposed at temperatures below 150°, water being the only volatile product formed. At the same time, the acidity sinks to half the original value; in the presence of a trace of sulphuric acid, the acidity can be reduced to one-quarter of the original value, but completely neutral products are never obtained.

Polyricinoleic acids (ester-acids in which the alcoholic hydroxyl group of one molecule is esterified by the carboxyl group of a second molecule) are the sole products of the action of heat on ricinoleic acid. Such products are not uniform, but contain a mixture of difficultly or non-separable polyricinoleic acids with more or less of the original acid. Polyricinoleic acids of high molecular weight are insoluble in alcohol, whilst their barium salts resemble amber and are soluble in ether; those of lower molecular weight are soluble in alcohol, whilst their barium salts dissolve sparingly in ether. A complete separation of the individual polyricinoleic acids was not achieved.

The effect of a variety of substances on the course of the reaction has been investigated. Chlorides of organic acids and neutral salts which do not yield free acid under the conditions of the experiments have but little effect. Traces of strong acids, particularly sulphuric acid, act as positive catalysts, whilst organic bases have the opposite action.

Ricinelaidic acid behaves in the same manner as ricinoleic acid except that it is more readily decomposed by heat. H. W.

Neodymium Oxalate and Some New Compounds of Europium. CHARLES JAMES and J. E. ROBINSON (*J. Amer. Chem. Soc.*, 1913, **35**, 754—759).—A study of the solubility of neodymium

oxalate in solutions of neodymium nitrate of various concentrations at 25° has shown that only one hydrate of neodymium oxalate,

$$Nd_2(C_2O_4)_3,11H_2O,$$
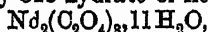
is stable under these conditions. Evidence was obtained of the formation of an oxalonitrate.

Europium *formate*, $Eu_2(CO_2H)_6$, *quinate*,

$$Eu_2[C_6H_7(OH)_4 \cdot CO_2]_6,12H_2O,$$

pyromucate, $Eu_2(C_4H_3O \cdot CO_2)_6,2H_2O$, and m-*nitrobenzenesulphonate*,

$$Eu_2(NO_2 \cdot C_6H_4 \cdot SO_3)_6,6H_2O,$$

are described.   E. G.

The Action of Ultraviolet Rays on Aldehydes. ADOLF FRANKE and ERNST POLLITZER (*Monatsh.*, 1913, 34, 797—809).—When exposed to the radiation from a quartz-mercury lamp, formaldehyde solutions undergo partial decomposition into carbon monoxide, carbon dioxide, hydrogen and methane, and partial polymerisation to glycollaldehyde and higher products (Pribram and Franke, A., 1912, i, 412); the higher aldehydes have been observed to form carbon monoxide, hydrogen, and the hydrocarbon corresponding with the radicle to which the aldehyde group was previously attached (Berthelot and Gaudechon, A., 1910, ii, 814). A re-investigation of the behaviour of the homologues of formaldehyde indicates that they decompose mainly according to the equation $R \cdot CHO = RH + CO$; at the same time condensation takes place to some extent accompanied by polymerisation to resinous substances ; no pure condensation product could be isolated. Under the conditions of the experiments, in which moisture and atmospheric oxygen were excluded, no formation of acids or of esters could be dectected, so that the earlier suggestion of Pribram and Franke (*loc. cit.*) that the formic acid obtained in the illumination of formaldehyde solution is produced by the hydrolysis of previously formed methyl formate is hardly probable. From the behaviour of crotonaldehyde, which like benzaldehyde and cinnamaldehyde gives practically no liberation of gas, it appears that the decomposition expressed by the above equation is characteristic of the saturated aliphatic aldehydes.

The aldehyde under examination was contained in a quartz flask of approximately 100 c.c. capacity which was filled to the neck, any evolved gas being collected over water or mercury ; the mercury lamp was at a distance of 2 to 3 mm. from the flask, but the temperature of the aldehyde never exceeded 50°.

The substances examined were heptaldehyde, *iso*butaldehyde, propaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde, and cinnamaldehyde. Crotonaldehyde gave only the formation of a resinous substance, whilst the two aromatic aldehydes gave merely red, non-volatile products. The illumination ranged from one to ten days in various cases ; only a relatively small proportion of each aldehyde underwent conversion.   D. F. T.

Action of Hydrazine and Hydrazine Derivatives on Molten Chloral Hydrate. GUSTAV KNOPFER (*Monatsh.*, 1913, 34, 769—777). —Hydrazine reacts with solutions of chloral hydrate, giving an additive product, $CCl_3 \cdot CH(OH) \cdot NH \cdot NH_2$, chloralhydrazine (compare A., 1911,

i, 1033); it is now found that if hydrazine sulphate or hydrochloride is dissolved in an excess of molten chloral hydrate, needles of a *substance*, m. p. 187° (decomp.), separate, but the composition is $C_4H_7ON_2Cl_6$, instead of $C_4H_4ON_2Cl_6$, which would be expected from a simple condensation such as that producing anhydrochloralurethane (Feist, A., 1912, i, 566).

The reaction product of benzalazine and chloral hydrate, obtained in a manner similar to the above, has the composition $C_9H_7ON_2Cl_3$, which is again two hydrogen atoms short of the formula for a substance produced by mere condensation; the *substance*, leaflets, m. p. 185°, when heated with potassium hydroxide solution loses a molecule of hydrogen chloride, giving a *substance*, $C_9H_6ON_2Cl_2$, needles, m. p. 86°. The former of these substances is not identical with the isomeric chloralbenzoylhydrazone, $CCl_3 \cdot CH:N \cdot NHBz$ (Stollé, A., 1905, i, 94), and, as it does not yield chloroform when treated with alkali, it is not likely to be the trichloroacetylhydrazone of benzaldehyde,

$$CCl_3 \cdot CO \cdot NH \cdot N:CHPh.$$

The loss of the two hydrogen atoms in each case is possibly due to a similar cause to the loss observed by Pinner (A., 1894, i, 385) where the continued action of hydrazine on the imino-ester of benzoic acid gives rise to $NH:CPh \cdot NH_2$, $NH:CPh \cdot NH \cdot NH \cdot CPh:NH$, and

$$CPh\underset{NH \cdot NH}{\overset{N \longrightarrow N}{<\quad>}}CPh$$
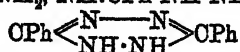
successively. The structure of the above products, however, remains for the present unsettled.   D. F. T.

Keto-enolic Tautomerism. VIII. Formation of Derivatives of Tautomeric Compounds. KURT H. MEYER (*Annalen*, 1913, 398, 49—65. Compare A., 1912, i, 940, 941).—To the terms "tautomerism," introduced by Laar in connexion with his oscillation theory, and "desmotropy" some confusion has become attached in the course of time and with the increase in the number of examples. The author proposes the following definitions. A substance exhibits tautomerism when it yields two series of derivatives obtained from two isomeric forms differing in the position of a hydrogen atom, and of one or more double linkings. According to the nature of the two isomeric forms, special cases of tautomerism are : (i) desmotropy—the free compounds corresponding with both forms are capable of separate existence or can be separately detected; (ii) pseudomerism—the tautomeric substance is known in only one form, the constitution of which can be determined by methods independent of tautomerism, and which can yield by addition or substitution derivatives of both forms ; the other form is unknown and its existence cannot be detected by any method ; (iii) cryptomerism—the substance is known in only one form, the constitution of which cannot be definitely determined (by methods independent of tautomerism).

Many reactions of desmotropic substances are explained readily by the desmotropy ; each form yields derivatives of its own type by ordinary double decomposition and usually one form reacts, the other being changed to the first by the reagent present. In other reactions the explanation is not so simple ; the tautomeric

substance yields a mixture of derivatives of both forms or only one substance, which is generally a derivative of the non-reacting form, for example, the formation of a brominated ketone by the bromination of an enol. Two theories are existent to explain such cases. The substitution theory claims that a substance can only yield derivatives of its own peculiar constitution, and that the production of a derivative of the other form must be due to a transformation of the tautomeride which precedes the substitution. The addition theory of Michael and of Nef assumes that by the direct addition of a reagent and subsequent elimination of a different molecule, a tautomeride of one form can yield derivatives of the other type.

Evidently the test of the two theories lies in the answer to the question, which of the two forms reacts? This answer can only be obtained by an examination of the behaviour of separately stable desmotropic substances. The author quotes numerous examples from his own work, and from that of Dimroth, Hinsberg, Hantzsch, and Herzig and Wenzel to show that the enolic modification is the reactive form, and that, therefore, the additive theory is probably correct.

[With S. LENHARDT.]—Keto-enolic desmotropes and also tautomerides which are known only in the ketonic or the enolic modifications condense with aldehydes (1 or 2 mols.), the resulting compounds losing water in various ways. In order to ascertain whether the ketonic or the enolic modification reacts with the aldehyde, the two desmotropic modifications of methyl mesityl oxide oxalate have been treated with benzaldehyde in the presence of a little piperidine. The ketonic modification, methyl $\alpha\gamma$-diketo-ϵ-methyl-Δ^δ-hexene-α-carboxylate, m. p. 67°, is unchanged, but the enolic modification, methyl α-hydroxy-γ-keto-ϵ-methyl-$\Delta^{\alpha\delta}$-hexadiene-α-carboxylate, is converted into the *lactone*,

$$\begin{array}{c} O \cdot CHPh \\ CO\text{---}CO \end{array}\!\!\!>\!\!CH \cdot CO \cdot CH\!:\!CMe_2,$$ m. p. 160°, colourless needles, which

does not react with ferric chloride or with alcoholic bromine, and is only slowly attacked by potassium permanganate, and is, therefore, the ketonic modification; the enolic form,

$$\begin{array}{c} O \cdot CHPh \\ CO\text{---}CO \end{array}\!\!\!>\!\!C\!:\!C(OH) \cdot CH\!:\!CMe_2,$$
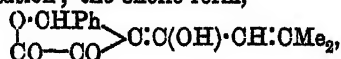
obtained by dissolving the ketonic modification in cold alcoholic sodium ethoxide, diluting with water, and acidifying, has m. p. 144°, then solidifies and has m. p. 160°, reacts with alcoholic bromine or ferric chloride, and is soluble in alkalis. By prolonged boiling with alcohol and a little piperidine, the enol is converted into the ketonic form; the same change occurs when the fused enol solidifies.

The authors believe that in all desmotropic and tautomeric compounds, condensation occurs by means of the enolic modification.

<div align="right">C. S.</div>

The Characterisation of Chloro-ketones. EDMOND E. BLAISE (*Compt. rend.*, 1913, **156**, 1549—1551).—The most suitable method of characterising the chloro-ketones is to convert them into their semicarbazones under definite conditions, the ordinary methods being unsatisfactory. Semicarbazide hydrochloride (1 to 1·5 mols.) is dis-

solved in water and the chloro-ketone added, when the semicarbazone is rapidly formed, the only exception being methyl trichloromethyl ketone, which requires a cold alcoholic solution of free semicarbazide. Care must be taken in purification. After filtering and washing with water the semicarbazone is heated with an excess of benzene to below 50°, a little anhydrous sodium sulphate is added, the liquid filtered and left for crystallisation. The semicarbazones of the α-chloro-ketones are readily converted into those of the α-hydroxy-ketones by contact with aqueous potassium carbonate for a few hours, and into those of the α-acetoxy-ketones by warming for a few minutes with an alcoholic solution of anhydrous sodium acetate, thus giving three means of identification of the original ketone.

Dichloro-ketones of the type $CHCl_2 \cdot CO \cdot R$ give a normal semicarbazone, but those of the type $CRCl_2 \cdot CO \cdot R'$ give disemicarbazones, $R \cdot C(N \cdot CH_8ON_2) \cdot C(N \cdot CH_8ON_2)R'$, which are insoluble in organic solvents, except formic and acetic acids.

The following semicarbazones and disemicarbazones have been prepared :

Methyl trichloromethyl ketone semicarbazone, $CCl_8 \cdot CMe \colon N \cdot CH_8ON_2$, fine needles, m. p. 140°.

Dichloromethyl ethyl ketone semicarbazone, m. p. 142°.

Ethylglyoxaldisemicarbazone, $CH \colon (N \cdot CH_8ON_2) \cdot CEt \colon (N \cdot CH_8ON_2)$, m. p. above 230°.

Dimethyldiketone disemicarbazone,
$$CMe \colon (N \cdot CH_8ON_2) \cdot CMe \colon (N \cdot CH_8ON_2),$$
a white, crystalline powder, m. p. above 230°, soluble only in formic acid.
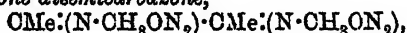
Chloromethyl chloroethyl ketone semicarbazone,
$$CH_2Cl \cdot C \colon (N \cdot CH_8ON_2) \cdot CHClMe,$$
m. p. 140°.
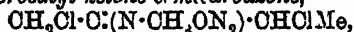
Methyl chloroethyl ketone semicarbazone, micaceous plates, m. p. 148°, which with carbonic acid gives the *semicarbazone*, m. p. 202°, of the corresponding hydroxy-ketone, and with sodium acetate gives *methyl acetoxyethyl ketone semicarbazone*, $CMe \cdot C \colon (N \cdot CH_8ON_2) \cdot CHAcMe$, m. p. 161°.

Chloromethyl propyl ketone semicarbazone, m. p. 157°.   W. G.

Mannitol Esters of Sulphuric Acid. W. R. BLOOR (*J. Amer. Chem. Soc.*, 1913, 35, 784—794).—In preparing certain mannitol esters of the higher fatty acids by heating the substance with sulphuric acid at 70° (A., 1910, i, 538 ; 1912, i, 532 ; ii, 365) unsatisfactory results were obtained, and for this reason a study has been made of the action of concentrated sulphuric acid on mannitol at 39°, 49°, 56°, and 65°.

When mannitol is dissolved in concentrated sulphuric acid, the disulphate is the principal compound produced, but a portion of the mannitol is dehydrated to the form $C_6H_6O(OH)_2$. At low temperatures a lævorotatory ester is produced, but at higher temperatures dextrorotatory compounds are formed together with derivatives which have lost part of their capacity to combine with acid groups. In the presence of the higher fatty acids, esters are produced, presumably

with the mannitol anhydride, but during the processes of separation they are hydrated to mannide and mannitan forms. E. G.

Acetyl-Halogen Sugar Derivatives. W. SLOAN MILLS (*Rep. Brit. Assoc.*, 1912, 444—445).—β-Iodoacetodextrose (E. and H. Fischer, A., 1910, i, 716) may be prepared by the action of dry hydrogen iodide on β-penta-acetyldextrose dissolved in dichloromethane. It is recrystallised rapidly from alcohol. Copper hydride reduces it, yielding a compound $C_{26}H_{44}O_{19}$

β-*Acetyliodogalactose* is prepared in the same manner from β-penta-acetylgalactose, and has m. p. 93—94°. Octoacetylmaltose yields an iodo-derivative, m. p. 62—66°. Acetyliodolactose, from acetyl-lactose, has m. p. 142°. C. H. D.

Gentiobiose. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, 85, 399—407).—Octa-acetylgentiobiose crystallises well and is relatively easily isolated from highly impure crude products. Acetylation may thus be used to obtain gentiobiose from plant products, and its preparation from gentian roots is described. *Octa-acetylgentiobiose* sinters at 192°, m. p. 195°, $[a]_D^{20}$ − 5 6°. Gentiobiose is equivalent to 130 c.c. of Fehling's solution, maltose reducing 128·5 c.c. The phenylosazone crystallises in citron-yellow, stellate needles, or from hot water in short, pointed prisms, m. p. 160—170° (decomp.), $[a]_D^{20}$ − 76·1° in pyridine and alcohol. E. F. A.

Deflocculation of Starch and Solution of Dextrose. GIOVANNI MALFITANO and (Mlle.) A. MOSCHKOV (*Compt. rend.*, 1913, 156, 1681—1684. Compare this vol., i, 593).—A further discussion of the difference between the phenomenon of deflocculation of starch and that of the solution of dextrose and a description of the difference in behaviour of solutions of these pseudo-crystals of starch and crystals of dextrose under different conditions. W. G.

Diastatic Degradation of Starch. WILHELM BILTZ (*Ber.*, 1913, 46, 1532—1536).—The degradation of potato starch under the influence of enzymes has been studied, the course of the reaction being followed qualitatively by the iodine reaction and quantitatively by the withdrawal of portions of the solution at definite intervals, addition of boiling water, and precipitation of the dextrins by the addition of so much alcohol that the mixture contained 80—90% of the latter, the treatment being repeated until the product was free from sugar. The approximate mean molecular weight of the dextrins was then determined by measurement of the viscosity of their aqueous solution (compare this vol., i, 593).

The following are the main results obtained :

The diastatic degradation of starch to sugar takes place with intermediate formation of erythrodextrins and achroodextrins which are themselves ultimately transformed into sugar. The velocity of saccharification of the achroodextrins is smaller than that of the erythrodextrins, and this is again smaller than that of the amylodextrins.

The existence of erythrodextrins is established.

The mean molecular weights for the achroodextrins is about 3700 ; for the erythrodextrins, 6200—7000 ; for the amylodextrins, above 10,000. Since purified specimens of achroodextrin I, achroodextrin II, and erythrodextrin IIα have molecular weights 1800, 1200 and 3000 respectively, it would appear that, besides these and the amylodextrins, other dextrins of high molecular weight must exist which are indifferent towards iodine and belong to the class of achroodextrins.

Philoche's determinations of the velocity of the conversion of starch into sugar (A., 1908, i, 712 ; ii, 470) show that this rapidly diminishes at first, but then becomes constant when the reaction appears to be unimolecular. The author's experiments show that the first phase of the reaction is complicated by the presence of amylo- and erythro-dextrins in the mixture, and that reaction only follows a simple law when only one type of substances, namely, the achroodextrins, are undergoing saccharification.　　　　　　　　　　　　　　　H. W.

Partial Hydrolysis of Cellulose. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, **85**, 180—191).—On treatment of cellulose with strong sulphuric acid a mixture of various depolymerised products is obtained. Even after prolonged treatment, cellobiose acetate is obtained on acetolysis and not dextrose pentacetate. Crystalline products were not obtained on acetolysis of xylan and mannan preparations or of chitin.

　　　　　　　　　　　　　　　　　　　　　　　　　E. F. A.

Chemical Composition of Cork Substance. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, **85**, 173—179).—Cork when treated by Cross and Bevan's method with chlorine yields a product, which in its external properties and solubility resembles cellulose, but on treatment with acetic anhydride and sulphuric acid by Skraup's method gave no cellobioseocta-acetate. One hundred grams of cork meal contained about 4 grams of this cellulose-like product.　　　　　E. F. A.

Betonicine and Turicine. ALBERT KUNG and GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, **85**, 209—216).—The mixture of betaines in *Betonica officinalis* has been resolved into two isomerides, a lævorotatory base betonicine, and a dextrorotatory base turicine. Both are betaines of the natural hydroxyproline, and on exhaustive methylation of this compound the same mixture of the two betaines is obtained as exists in *Betonica officinalis*, *Stachys silvatica*, etc. According to the method of isolation sometimes one and sometimes the other isomeride has been isolated, in reality both are present.

Betonicine crystallises in four-sided, stunted pyramids, m. p. 243—244° (decomp.). It reacts neutral, tastes sweet, and has $[α]_D^{15} - 36.6°$. The *hydrochloride* crystallises in lustrous prisms, m. p. 222—223° (decomp.), $[α]_D^{15} - 24.79°$. The *aurichloride* separates in dull yellow-coloured plates aggregated in fan-shaped clusters, m. p. 242°. The *platinichloride* forms short prisms, m. p. 226°.

Turicine crystallises in long, transparent, lustrous, flat prisms, or in slender, glistening needles, m. p. 249° (decomp.), $[α]_D + 36.26°$. It tastes sweet and is not hydroscopic. The *hydrochloride* crystallises in slender, lustrous needles, m. p. 223°, and reacts acid, $[α]_D + 24.65°$.

The *aurichloride* is a yellow powder crystallising in obliquely-cut, lustrous prisms, m. p. 232°. The crystalline *platinichloride* has m. p. 223°.   E. F. A.

Synthesis of Betonicine and Turicine. ALBERT KUNG (*Zeitsch. physiol. Chem.*, 1913, 85, 217—224. Compare preceding abstract).— γ-Hydroxyproline prepared by E. Fischer's method from gelatin can be methylated by means of potassium hydroxide in methyl alcohol and methyl iodide. The product, hydroxyprolinebetaine,

$$\mathrm{HO\cdot CH}\Big\langle {}^{CH_2\cdot CH—CO}_{CH_2\cdot NMe_2\cdot O} \text{ ,}$$
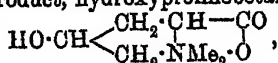
is a mixture of betonicine and turicine in equal quantities. The nature of the isomerism between these two betaines has not been established.
                                                                      E. F. A.

Compounds of Hexamethylenetetramine with Various Silver Salts. LUDWIG VANINO and PAULA SACHS (*Arch. Pharm.*, 1913, 251, 290—293. Compare Grützner, A., 1899, i, 6).—The authors have prepared the compound of hexamethylenetetramine with silver nitrate, obtained by Grützner (*loc. cit.*), and also *compounds* with the following silver salts: silver fluoride, $C_6H_{12}N_4,AgF,3H_2O$, slender needles; silver chloride, B,4AgCl, prismatic crystals (compare Délepine, A., 1895, i, 261); silver bromide, B,3AgBr, microscopic crystals; silver iodide, B,3AgI, amorphous; silver chlorate, $B,AgClO_3,H_2O$, amorphous, explodes on warming; silver oxalate, $B,Ag_2C_2O_4$; globular masses of slender needles.   T. A. H.

The Methylation of Glycine by means of Formaldehyde. WALTHER LÖB (*Biochem. Zeitsch.*, 1913, 51, 116—127).—If formaldehyde is allowed to act on glycine in neutral solution in the cold, a compound, $CH_2:N\cdot CH_2\cdot CO_2H$, is formed, with separation of the elements of water, which under the influence of acids or alkalis readily undergoes scission again into formaldehyde and glycine. If, however, the substances are allowed to act on one another in hot acid solution, a stable *methylenediglycine*, $CH_2(NH\cdot CH_2\cdot CO_2H)_2$, is formed, which can be readily isolated in the form of a dihydrochloride, from which, by means of silver oxide, the free base can be obtained in platelets, melting about 199°. In alkaline solution, formaldehyde does not act on glycine. If formaldehyde in the presence of acid and zinc is allowed to act on glycine (at 100°), a mixture of sarcosine and dimethylaminoacetic acid is produced. The mechanism of this reaction is explained by assuming that methylenediglycine is reduced to a mixture of an equal number of molecules of methylglycine and glycine. By the action of formaldehyde on the former, methylenedi(methylglycine) can be produced, which, on reduction, yields an equal number of molecules of dimethyl- and monomethyl-glycines.   S. B. S.

Behaviour of α-Amino-acids and Polypeptides to Neutral Salts. PAUL PFEIFFER and J. VON MODELSKI (*Zeitsch. physiol. Chem.*, 1913, 85, 1—34. Compare A., 1912, i, 949).—The compounds of lithium chloride or bromide with glycine of the composition
$$LiX,NH_2\cdot CH_2\cdot CO_2H,H_2O$$

are readily prepared by evaporating an aqueous solution of the components until crystallisation begins. They form colourless needles, m. p. 136° (the chloride) and 175—176° (the bromide) respectively.

The compounds of the type $LiX,2NH_2\cdot CH_2\cdot CO_2H,H_2O$ are obtained by crystallising rapidly at room temperature from strong solutions after inoculation. They crystallise in colourless, transparent plates, m. p. 186—190° (the chloride) and 223° (the bromide).

The compound of lithium chloride and alanine,
$$LiCl,NH_2\cdot CHMe\cdot CO_2H,H_2O,$$
has m. p. 128—129°.

Monoglycine calcium chloride, $CaCl_2,NH_2\cdot CH_2\cdot CO_2H,3H_2O$, forms tiny, lustrous plates, which do not melt. *Diglycine calcium chloride*, $4H_2O$, crystallises in long, colourless needles. *Triglycine calcium chloride* separates in lustrous, transparent platelets which do not melt at 250°. *Triglycine lanthanum chloride*,
$$LaCl_3,3NH_2\cdot CH_2\cdot CO_2H,3H_2O,$$
forms colourless, transparent, prismatic needles.
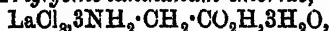
Monoalanine lithium chloride, $LiCl,NH_2\cdot CHMe\cdot CO_2H,H_2O$, crystallises in colourless, lustrous platelets, m. p. 127—128°. *Dialanine calcium chloride*, $3H_2O$, yields colourless, transparent needles, m. p. 77° to a viscid, clear liquid.

Monodiglycylglycine calcium chloride,
$$CaCl_2,NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,3H_2O,$$
separates in well-formed, colourless, transparent platelets.
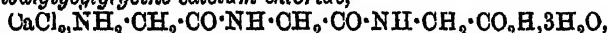
Monobetaine potassium bromide, $KBr,C_5H_{11}O_2N,2H_2O$, crystallises in transparent, tabular plates, which soften completely at 90—93°, m. p. about 110°. *Monobetaine potassium iodide* forms long, thin, colourless plates consisting in part of parallel, intergrown, flat needles, which sinter at 100°, begin to melt at 115°, and form a clear liquid at 140°. *Dibetaine potassium iodide* $KI,2C_5H_{11}O_2N,2H_2O$, forms colourless, tabular crystals with oblique faces, m. p. 148°. *Monobetaine barium chloride*, $4H_2O$, crystallises in long, thin, colourless, prismatic needles. *Monobetaine barium bromide*, $4H_2O$, also separates in similar needles.

The constitution of the salts described is discussed; they are regarded as amphi-salts in which both the basic and acid groups of the amino-acid are neutralised.   E. F. A.

Methyl Derivatives of δ-Aminovaleric Acid and *dl*-Ornithine. EMIL FISCHER and MAX BERGMANN (*Annalen*, 1913, **398**, 96—124).— By hydrolysis with hydrochloric acid, D 1·19, in a sealed tube in the water-bath, δ-*m*-nitrobenzoylamino-α-methylaminovaleric acid (A., 1909, i, 793) readily yields δ-*amino-α-methylaminovaleric acid dihydrochloride*, $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NHMe)\cdot CO_2H,2HCl$, m. p. 207—210° (decomp., corr.), colourless plates or prisms, which forms a precipitate with phosphotungstic acid, but not with potassium bismuth iodide even in considerably concentrated solutions. From the dihydrochloride, the *picrate*, $C_6H_{14}O_2N_2,2C_6H_3O_7N_3$, m. p. 205—206° (decomp., corr.), and the *platinichloride*, $C_6H_{14}O_2N_2,H_2PtCl_6,H_2O$ (or $4H_2O$), decomp. 218° (corr.), when anhydrous, have been prepared.

By treating an aqueous solution of the dihydrochloride with silver

sulphate, removing the excess of silver by hydrochloric acid and the sulphuric acid by barium hydroxide, and evaporating the filtrate at 10—20 mm., all the operations being performed in an atmosphere of carbon dioxide, δ-*amino-a-methylaminovaleric acid*, m. p. 82—100°, is obtained as a crystalline mass. Its aqueous solution reacts strongly alkaline, precipitates ferric hydroxide, and dissolves precipitated copper hydroxide.

By hydrolysing *dl*-benzoylornithine with boiling hydrochloric acid (D 1·19) and treating the resulting *dl*-ornithine with 2N-sodium hydroxide and benzenesulphonyl chloride (3 mols.) at 46—48°, and acidifying, aδ-*dibenzenesulphonyldiaminovaleric acid* (dl-*dibenzenesulphonylorni-thine*), $C_{17}H_{20}O_6N_2S_2,H_2O$, m. p. 155—157° (corr., anhydrous), micro-scopic needles, is obtained. By treatment with 2N-sodium hydroxide and methyl iodide at 65°, it yields, after acidification, aδ-*dibenzenesul-phonyldimethyldiaminovaleric acid*,

$$SO_2Ph\cdot NMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NMe\cdot SO_2Ph)\cdot CO_2H,$$
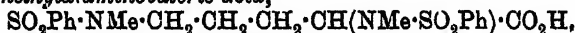
m. p. 141—142° (corr.), microscopic plates, by the hydrolysis of which by hydrochloric acid (D 1·19) at 100° is obtained N-*dimethylornithine-*aδ-*dimethyldiaminovaleric acid*), $NHMe\cdot[CH_2]_3\cdot CH(NHMe)\cdot CO_2H$, which is isolated by precipitation with phosphotungstic acid; the *hydro-chloride*, $C_7H_{16}O_2N_2,2HCl$, and *platinichloride*, $C_7H_{16}O_2N_2,H_2PtCl_6$, m. p. 220° (decomp., corr.), are described, and the *aurichloride* and *picrate* are mentioned. A 0·5% aqueous solution of dimethylornithine dihydrochloride and aqueous potassium bismuth iodide yield a brick-red precipitate after a few hours.

dl-Ornithine, obtained by the hydrolysis of δ-benzoylornithine, has been isolated in a crystalline state.

δ-Benzenesulphonylaminovaleric acid, 2N-sodium hydroxide, and methyl iodide at 63—65° yield, after acidification, δ-*benzenesulphonyl-methylaminovaleric acid*, $SO_2Ph\cdot NMe\cdot[CH_2]_4\cdot CO_2H$, m. p. 70—71° (corr.), colourless needles or prisms, by the hydrolysis of which by hydrochloric acid (D 1·19) is obtained δ-*methylaminovaleric acid*, m. p. 121—122° (corr.), needles or prisms, which is isolated by means of phosphotungstic acid. The acid is very hygroscopic, and its aqueous solution gives immediately a brick-red precipitate with potassium bismuth iodide; the *picrate*, $C_6H_{13}O_2N,C_6H_3O_7N_3,H_2O$, has m. p. 70—71° (corr.). At 130—160°, δ-methylaminovaleric acid loses water and is converted into

1-*methyl-2-piperidone*, $NMe\!\!<\!\!^{CO-CH_2}_{CH_2\cdot CH_2}\!\!>\!\!CH_2$, b. p. 94—95° (corr.)/ 9 mm.

3-Amino-2-piperidone, prepared from ornithine, reacts readily with benzaldehyde to form the *benzylidene* compound,

$$CHPh\!:\!N\cdot CH\!\!<\!\!^{CO-NH}_{CH_2\cdot CH_2}\!\!>\!\!CH_2,$$
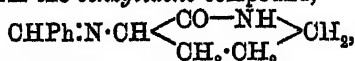
m. p. 140—142° (corr.), almost colourless crystals.

Glycine, *p*-toluenesulphonyl chloride, and 2N-sodium hydroxide at 67—70° yield, after acidification, p-*toluenesulphonylglycine*, $C_9H_{11}O_4NS$, m. p. 149—150° (corr.), slender needles, which is converted by 3N-sodium hydroxide and methyl iodide at 67° and subsequent

acidification into p-*toluenesulphonylsarcosine*, $C_{10}H_{13}O_4NS$, m. p. 150—152° (corr.), by the hydrolysis of which sarcosine is obtained.

The reaction of alcoholic sodium ethoxide, α-chloro-γ-bromopropane, and ethyl malonate in the presence of ether leads to the production of *ethyl γ-chloropropylmalonate*, $CH_2Cl \cdot CH_2 \cdot CH_2 \cdot CH(CO_2Et)_2$, b. p. 154—155° (corr.)/17 mm., which reacts with bromine in chloroform to form *ethyl bromo-γ-chloropropylmalonate*

$$CH_2Cl \cdot CH_2 \cdot CH_2 \cdot CBr(CO_2Et)_2,$$
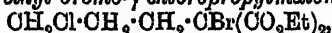
b. p. 175—176° (corr.)/17 mm. Ethyl γ-chloropropylmalonate and 33% aqueous methylamine react at the ordinary temperature to form *γ-chloropropylmalonmethylamide*, $CH_2Cl \cdot CH_2 \cdot CH_2 \cdot CH(CO \cdot NHMe)_2$, m. p. 158—162° (corr.), leaflets or needles.

A by-product in the preparation of ethyl γ-chloropropylmalonate under certain conditions is *ethyl di-γ-chloropropylmalonate*,

$$C(CH_2 \cdot CH_2 \cdot CH_2Cl)_2(CO_2Et)_2,$$
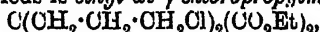
m. p. 51—52°, b. p. 195—197° (corr.)/14 mm., flattened crystals, which is converted by methyl alcoholic ammonia at 100° into a *substance*, $C_9H_{14}O_2N_2$, m. p. 330° (decomp., corr.), colourless, microscopic prisms, which is probably *bis-2-piperidone*-3 : 3'-*spiran*,

$$CH_2 \underset{NH-CO}{\overset{CH_2 \cdot CH_2}{<}} C \underset{CO-NH}{\overset{CH_2 \cdot CH_2}{<}} CH_2.$$
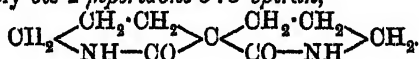
O. S.

The Oxidative Degradation of a Synthetic Tripeptide. OTTO EISLER (*Biochem. Zeitsch.*, 1913, 51, 45—52).—By the oxidation of alanylglycylglycine with calcium permanganate, using as much of the latter as is equivalent to 8—10 atoms of oxygen to one molecule of the peptide, an acid in the form of a crystalline calcium salt was isolated, the formula of which corresponded approximately with

$$C_6H_5O_7N_3Ca,6H_2O.$$
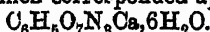
On hydrolysis by acids, one molecule gives rise to two molecules of oxalic acid. Two alternative formulæ are suggested by the author.

S. B. S.

Anhydride Formation with a Diaminohydroxy-acid. MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1913, 34, 781—786). —It has been shown (Kohn, A., 1908, i, 819; Kohn and Bum, A., 1910, i, 136) that *iso*hexan-δ-ol-β-one on treatment with potassium cyanide and ammonium chloride, or the hydrochloride of an amine, gives rise to an aminolactone. When equimolecular quantities of *iso*hexan-δ-ol-β-one, ethylenediamine dihydrochloride, potassium cyanide, and potassium hydroxide are heated together with a little water at 60° for five to six hours, and the resulting nitrile hydrolysed by treatment with concentrated hydrochloric acid, a *substance*, $C_9H_{18}O_2N_2$, prismatic crystals, m. p. 174°, is obtained, which gives a crystalline *picrate*,

$$C_9H_{18}O_2N_2,C_6H_3O_7N_3,$$
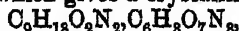
m. p. 154°, and an *oxalate*, $C_9H_{18}O_2N_2,2C_2H_2O_4,\tfrac{1}{2}H_2O$, tablets, m. p. 160° (decomp.).

The structure of the substance is probably that of a diaminolactone or of a hydroxylactam, but the point is at present undecided.

D. F. T.

The Electrolytic Formation of Carbamide and Acetamidine Nitrate. FRITZ FICHTER, KARL STUTZ, and FRITZ GRIESHABER (*Verhand. Naturfors. Ges. Basel*, 1912, **23**, 222—263).—It is shown that small quantities of carbamide are produced by the electrolysis of solutions of ammonium carbamate. The best yields, which are nevertheless very small, are obtained when the anode current density (C_a) lies between 0·130 and 0·555 ampere per sq. cm. Between these values the yield is practically constant and amounts to about 0·60 gram per 100 ampere-hours. It is shown that the yield is increased if the concentration of the carbamate is increased, and also increase of free ammonia increases the yield, the latter factor being of much more importance than the former. The best yield is obtained with a solution containing 12 gram-equivalents of ammonia and 8 gram-equivalents of ammonium carbamate. It is also shown that carbamide is decomposed by the oxidising action of the current and converted into ammonium nitrate, and that the amount of decomposition is greatest when there is no free ammonia present and that it decreases, rapidly as the concentration of ammonia is increased. The gases evolved at the anode were collected and analysed, and the relationship between their composition and the temperature and excess ammonia concentration determined. It is shown that at 18° with $C_a = 0·014$ ampere per sq. cm., the percentage of oxygen slowly decreases, whilst the nitrogen increases with the concentration of free ammonia up to 7 gram-equivalents per litre, and that on further increasing the free ammonia concentration the nitrogen increases rapidly until at 12 gram-equivalents per litre it has reached 100%. From a solution containing 9 gram-equivalents of ammonia the percentage of nitrogen in the gas was 24·8% at 6°, whilst at 18° it had increased to 99·1%. A theory is put forward to represent the electrolytic oxidation of ammonia which can be shortly represented by the scheme:

$$NH_3 \longrightarrow NH_2 \cdot OH \longrightarrow H_2N_2O_2$$
$$\downarrow$$
$$N_2O + H_2O$$

and

$$NH_4 \cdot ON:N \cdot OH \longrightarrow NH_4NO_3 \dashrightarrow NH_4NO_3$$
$$\downarrow$$
$$N_2 + H_2O$$
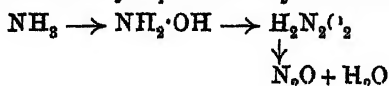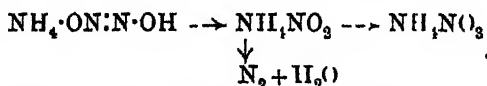
Nitrous oxide is found in the gases collected at the anode, and the other steps in the process are generally confirmed by the observations. The formation of carbamide by the electrolysis of ammonium carbamate is explained by the following scheme:

$$O:C(NH_2) \cdot ONH_4 + 2NH_2 \cdot OH = 2 \cdot O:CH \cdot NH_2 + H_2N_2O_2 + 2NH_3 + 2H_2O$$
$$O + NH_3 + O:CH \cdot NH_2 = NH_4 \cdot CO(NH_2) + H_2O$$
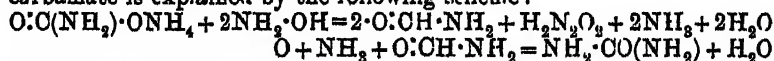
According to this, formamide is produced by the interaction of hydroxylamine, produced as above, and ammonium carbamate, and this is then electrolytically oxidised in the presence of ammonia to carbamide. In proof of this theory the authors quote the work of Jouve (A., 1899, i, 420), who showed that when carbon monoxide is heated with ammoniacal cuprous chloride, carbamide is produced. Further, Hofmeister and Halsey (A., 1898, ii, 529) have shown that a large number

of organic substances when treated with potassium permanganate in ammoniacal solution yield carbamide. These substances are all oxy-acids, ketones, and ketonic acids, that is, substances which give carbon monoxide on oxidation. Carbamide was next obtained by electrolysing a solution of ammonium acetate containing methyl alcohol; this is represented by

$$CH_3 \cdot OH \longrightarrow CO \longrightarrow H \cdot CO \cdot NH_2 \longrightarrow NH_2 \cdot CO \cdot NH_2.$$

When ethyl alcohol was electrolysed in ammoniacal solution a small quantity of acetamidine nitrate was obtained. It was found that the addition of ammonium nitrate increased the yield of the amidine nitrate, and that if no ammonium nitrate had been added, often there was no yield at all. The formation is represented by the scheme:

$$CH_3 \cdot CH_2 \cdot OH \longrightarrow CH_3 \cdot CHO + NH_3 \longrightarrow$$
$$CH_3 \cdot CH(OH) \cdot NH_2 + O + NH_3 \longrightarrow CH_3 \cdot C(NH)NH_2$$
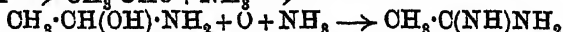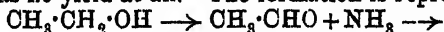
The authors show in confirmation of the above that aldehyde ammonia can be oxidised to the amidine by calcium permanganate, ammonium persulphate and hydrogen peroxide, and isolated provided that excess of ammonia and some ammonium nitrate are present. The corresponding propionamidine nitrate and butyramidine nitrate were obtained by the electrolysis of ammoniacal solutions of propyl and butyl alcohols respectively. In the case of butyl alcohol only the smallest yield was obtained, and with higher alcohols amidine nitrates could not be obtained in any case. J. F. S.

The Fixation of Nitrogen by Mixtures of Barium Oxide and Charcoal. THOMAS EWAN and THOMAS NAPIER (*J. Soc. Chem. Ind.*, 1913, **32**, 467—474).—The first set of experiments were carried out by heating a mixture of two parts of barium carbonate and one part of well-burned wood charcoal, contained in an iron boat, in a porcelain tube in a current of nitrogen. The results obtained were as follows (compare Kühling and Berkhold, A., 1908, i, 143): the absorption of nitrogen begins between 900° and 930°. The amount absorbed under the same conditions increases very rapidly with the temperature, for example, if 4 mols. of nitrogen are passed over 1 mol. of $BaCO_3$ in two hours, about 1% of the barium will combine with it at 930°, about 14% at 960°, and about 40% at 1000°. The greater part of the nitrogen fixed is in the form of cyanide. Under the conditions used by the authors, about 2·5% of the nitrogen used is fixed at 960° and about 10% at 1000°. The addition of quantities of potassium carbonate up to 11% seems to improve the results, but the improvement is no more than would be produced by a difference of 10—20° in temperature.

No cyanide is formed until some 30% of the barium carbonate has been converted into oxide, and the quantity of carbon monoxide in the gas has fallen to about 30%; the percentage of carbon monoxide falls steadily as the formation of cyanide progresses.

The authors draw the conclusion that the fixation of nitrogen is due to one or both of the reversible reactions: $BaO + 2C + N_2 \rightleftharpoons BaCN_2 + CO$, $BaO + 3C + N_2 \rightleftharpoons Ba(CN)_2 + CO$; and further experiments indicate that the barium compounds mix in the solid (or fused) mixture, so that the ratio of the partial pressures of carbon monoxide and nitrogen in

the gas when equilibrium is attained at any given temperature depends on the relative quantities of cyanide, cyanamide, and oxide in the mixture. The reaction appears to be arrested at half-conversion of the barium oxide, which may be explained by assuming the formation of a compound $BaO,Ba(CN)_2$, in which the barium oxide is much less active than in the free state.

Pure barium cyanide is readily obtained by suspending anhydrous barium hydroxide, in the form of a fine powder, in light petroleum, and adding an emulsion of the theoretical quantity of anhydrous hydrocyanic acid in light petroleum. It fuses at 600° and is distinctly volatile even at its melting point. The fused product contains barium cyanamide, the amount of which depends, among other things, on the temperature and the length of time the fusion is heated; the presence of finely divided iron in the cyanide increases the amount of cyanamide formed.

When barium ferrocyanide is heated in a vacuum or in an atmosphere of nitrogen, decomposition begins at about 500°, nitrogen is evolved, and a mixture of carbon, iron, and barium cyanide and cyanamide remains behind.

When mixtures of barium oxide, cyanide, and cyanamide are heated in nitrogen, the combined nitrogen passes more and more into the form of cyanide as the mixture is more and more diluted with barium oxide.

T. S. P.

Some Aliphatic Cyanoacetylamines. MARIA CLOTILDE BIANCHI (*Atti R. Accad. Sci. Torino*, 1912–1913, **48**, 654—659).—*Cyanoacetomethylamide*, $CN \cdot CH_2 \cdot CO \cdot NHMe$, is prepared with almost the theoretical yield by passing gaseous methylamine into an alcoholic solution of ethyl cyanoacetate; it crystallises in prisms, m. p. about 104—105°. *Cyanoacetoethylamide*, $CN \cdot CH_2 \cdot CO \cdot NHEt$, is similarly prepared and forms prismatic laminæ, m. p. 74—75°; it is oxidised by potassium permanganate at the ordinary temperature.

Dicyanoacetopropylenediamide, $(CN \cdot CH_2 \cdot CO \cdot NH)_2C_3H_6$, obtained by keeping a mixture of ethyl cyanoacetate and propylenediamine for twenty-four hours, crystallises in colourless needles, m. p. 161—162°.

Dicyanoacetotrimethylenediamide, $CH_2(CH_2 \cdot NH \cdot CO \cdot CH_2 \cdot CN)_2$, prepared by mixing ethyl cyanoacetate and trimethylenediamine, crystallises in slightly yellow needles, m. p. 163—165°.

Cyanoacetamide, after recrystallisation from ether, has m. p. 124—125°, which is higher than the m. p. given in the literature.

R. V. S.

Photochemical Synthesis of a New Compound, Carbonyl Cyanide, by means of Ultra-violet Rays. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, **156**, 1766—1768).—Carbon monoxide and cyanogen when mixed and subjected to the ultra-violet rays ($\lambda < 0.25\ \mu$) from a mercury-quartz lamp combine to form *carbonyl cyanide*, $CO(CN)_2$, a yellow, amorphous compound, which does not volatilise at 200°, but gives off small quantities of nitrogen. It is soluble in alkalis, giving a yellow solution, and slowly

undergoes hydrolysis on the addition of acid, giving carbon dioxide and hydrogen cyanide. It burns only very slowly in oxygen at a red heat.

<div align="right">W. G.</div>

[Potassium Manganicyanide.] JULIUS MEYER (*Zeitsch. anorg. Chem.*, 1913, **81**, 385—405).—See this vol., ii, 599.

Some Azides of Carbamic Acid. VI. E. OLIVERI-MANDALÀ and F. NOTO (*Gazzetta*, 1913, **43**, i, 514—520).—The azides described in this paper were prepared by the action of azoimide on carbimides. Methylcarbamazide can be obtained in this way. *Chloromethylcarbamazide* (from chloromethylcarbimide in benzene solution) decomposes rapidly on exposure to the air. Alcoholic ammonia converts it into a substance, $(C_2H_5ON_2Cl)_3$, having the composition of a *trimeride* of the *chloromethylcarbamide* to be expected; it decomposes above 300°, evolving hydrogen chloride.

Bromomethylcarbamazide is similarly obtained from *bromomethylcarbimide*, which can be prepared by Schroeter's method (A., 1909, i, 773); this azide is also very unstable. When it is treated with alcoholic ammonia, a *trimeric bromomethylcarbamide*, $(C_2H_5ON_2Br)_3$, is produced; it decomposes above 300°.

Propylcarbimide, prepared from silver cyanate and propyl iodide, has b. p. 82—85°. The *azide*, $C_4H_8ON_4$, has b. p. 85—86°/28 mm. When heated for two hours with aniline in alcoholic solution, it yields s-*phenylpropylcarbamide*, $C_{10}H_{14}ON_2$, m. p. 114—116°.

iso*Propylcarbamazide*, $C_4H_8ON_4$, crystallises in long needles, m. p. 44°. s-*Phenyl*isopropylcarbamide, $C_{10}H_{14}ON_2$, obtained from this azide, forms needles, m. p. 142—143°.

iso*Butylcarbamazide*, $C_5H_{10}ON_4$, has b. p. 94°/22 mm. s-*Phenyl*-isobutylcarbamide, $C_{11}H_{16}ON_2$, crystallises in small needles, m. p. 158°.

<div align="right">R. V. S.</div>

A New Class of Lipoid Arsenic Compounds. EMIL FISCHER and GEORG KLEMPERER (*Therapie der Gegenwart*, Jan., 1913; Reprint 8 pp.).—When behenolic acid is heated with arsenic trichloride and the product of action is afterwards treated with bases, an acid containing arsenic and chlorine in approximately equivalent quantities is formed. It has been obtained so far as a coloured oil, which is not sufficiently pure for analysis. The strontium salt, containing about 13% arsenic and 6% chlorine, has been employed under the name of elarson as a medicament containing arsenic in a relatively non-toxic form, and satisfactory therapeutic results are claimed for it in cases requiring treatment by arsenic.

<div align="right">S. B. S.</div>

Hydro-aromatic Substances. ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Rep. Brit. Assoc.*, 1912, 124—125).—See Crossley and Renouf, T., 1912, **101**, 1524; Crossley and Smith, P., 1912, 332.

<div align="right">C. H. D.</div>

Preparation of Several Dicyclohexylbutanes. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, **156**, 1430—1434. Compare A., 1912, i, 547, 617, 757).—By direct hydrogenation with reduced

nickel the authors have prepared five of the nine possible dicyclo-hexylbutanes, three being derivatives of *n*-butane and two of *iso*-butane; *aδ-dicyclohexylbutane*, $C_6H_{11}\cdot[CH_2]_4\cdot C_6H_{11}$, colourless crystals, m. p. 9°, b. p. 304—306° (corr.), D_0^{21} 0·8772, n_D^{21} 1·475, is obtained by the reduction of aδ-diphenylbutane.

Phenyl ethyl ketone reacts with magnesium benzyl chloride at 450° in the presence of thorium oxide to give phenylbenzylethylcarbinol, which by distillation under reduced pressure yields diphenyl-Δ^a-butylere, b. p. 296° (corr.), D_0^{18} 1·0124, n_D^{15} 1·593 (compare Klages and Heilmann, A., 1904, i, 487). This hydrocarbon on hydrogenation in the presence of slightly active nickel gives *aβ-diphenylbutane*, a colourless liquid, b. p. 285—287° (corr.), D_0^{18} 1·0092, n_D^{19} 1·587, which on further hydrogenation over very active nickel at 170° yields *aβ-dicyclohexylbutane*, a colourless liquid, b. p. 276—278° (corr.), D_0^0 0·9104, D_0^{18} 0·9084, n_D^{15} 1·500.

aa-Diphenyl - Δ^a - *butylene*, b. p. 295—297° (corr.), D_0^{16} 1·0039, n_D^{16} 1·595, obtained by the interaction of magnesium phenyl bromide and ethyl butyrate and subsequent dehydration, on hydrogenation at 150° with slightly active nickel yields *aa-diphenylbutane*, b. p. 286—288° (corr.), D_0^{18} 0·9748, n_D^{16} 1 554. If this hydrogenation is carried out at 250° the product is diphenylmethane, m. p. 27°, b. p. 262°, described by Klages and Heilmann (*loc. cit.*) as aa-diphenylbutane. The aa-diphenylbutane, now described, on hydrogenation at 170° with very active nickel yields *aa-dicyclohexylbutane*, b. p. 280—282° (corr.), D_0^0 0·8922, D_0^{16} 0·8842, n_D^{16} 1·485.

By the interaction of benzophenone and magnesium *iso*propyl iodide or by the action of magnesium phenyl bromide on ethyl *iso*butyrate, and subsequent dehydration of the carbinol formed, *aa-diphenyl-β-methylpropylene*, b. p. 293°, D_0^{16} 1·0240, n_D^{16} 1·596, is obtained, and this on gentle hydrogenation at 180° yields *aa-diphenyl-β-methylpropane*, b. p. 285—286° (corr.), D_0^{16} 0·978, n_D^{16} 1·560. This hydrocarbon by more active hydrogenation at 170° gives *aa-dicyclohexyl-β-methyl-propane*, b. p. 278—279° (corr.), D_0^0 0·9017, D_0^{16} 0·8906, n_D^{15} 1·492.

aγ-Diphenyl-β-methylpropylene, b. p. 304° (corr.), D_0^{16} 1 0181, n_D^{16} 1·593, obtained in the usual way from magnesium methyl iodide and dibenzyl ketone, on hydrogenation at 170° with very active nickel yields *aγ-dicyclohexyl-β-methylpropane*, b. p. 290—292° (corr.), D_0^0 0·8916, D_0^{19} 0·8840, n_D^{19} 1·484. W. G.

Partial Reduction of Aromatic Polynitro-compounds by Electrochemical Methods. III. Kurt Brand and Th. Eisen-menger (*J. pr. Chem.*, 1913, [ii], 87, 487—507. Compare A., 1906, i, 80 ; 1907, i, 755).—The present paper deals with the electrolytic reduction of 2 : 4 : 6-trinitrotoluene, 2 : 4-dinitroanisole, and 4-chloro-*m*-dinitrobenzene in alkaline, acid and almost neutral solution.

On reduction in alkaline solution at a mercury cathode, 4-chloro-*m*-dinitrobenzene yields 4-chloro-*m*-nitroaniline and 6-chloro-*m*-nitro-aniline, together with 2 : 4-dinitrophenol ; under the same conditions, 2 : 4-dinitroanisole is reduced to 5 : 5'-*dinitro-o-azoxyanisole*, which separates from benzene in slender, almost colourless leaflets, m. p. 209°.

The constitution of the azoxy-compound has been established by its

preparation from 5-nitro-2-methoxyphenylhydroxylamine by the action
of sodium hydroxide in alcoholic solution. The reduction of 2 : 4 : 6-
trinitrotoluene in alkaline solution yielded no definite product. In
hydrochloric acid solution and in the presence of cupric chloride,
2 : 4 : 6-trinitrotoluene is reduced at a copper cathode to 2 : 6-dinitro-p-
toluidine and 4 : 6-dinitro-o-toluidine.

The last-named compound forms orange-yellow crystals, which have
m. p. 135° and not 155° as given by Holleman and Böeseken (A., 1898, i,
303). It yields an *acetyl* derivative, crystallises in white needles,
m. p. 224°, and when diazotised and boiled with alcohol is converted
into 2 : 4-dinitrotoluene and 2 : 4-*dinitroindazole*,

$$C_6H_2(NO_2)_2 <^{CH}_{N}>NH,$$
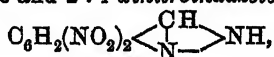
which crystallises in almost white needles, m. p. 203°, and dissolves in
aqueous alkalis, yielding yellow solutions.

On reduction in acid solution under the same conditions as given
above for 2 : 4 : 6-trinitrotoluene, 2 : 4-dinitroanisole yields 4-nitro-
o-anisidine (Meldola, Woolcott, and Wray, T., 1896, **69**, 1321), whilst
4-chloro-m-dinitrobenzene gives rise to 4-chloro-m-nitroaniline and
6-chloro-m-nitroaniline, which are separated by crystallisation of their
acetyl derivatives from alcohol.

In almost neutral solution, 2 : 4 : 6-trinitrotoluene is reduced at a
silver cathode to 2 : 6-dinitro-p-tolylhydroxylamine (Cohen and Dakin,
T., 1902, **81**, 27) and 4 : 6-*dinitro-o-tolylhydroxylamine*, which forms
light yellow crystals, m. p. 109°.

The constitution of 2 : 6-dinitro-p-tolylhydroxylamine has been
confirmed by its reduction with copper powder and hydrochloric acid
to 2 : 6-dinitro-p-toluidine, and conversion of the latter compound by
diazotisation and boiling with alcohol into 2 : 6-dinitrotoluene. When
boiled with strong hydrochloric acid, 2 : 6-dinitro-p-tolylhydroxylamine
yields 3 : 5 : 3′ : 5′-*tetranitro*-p-*azoxytoluene*, colourless needles, m. p.
216°; on treatment with phosphorus pentachloride in ethereal solution
it gives rise to 3 : 5 : 3′ : 5′-*tetranitro*-p-*azotoluene*, which crystallises in
orange needles, m. p. 248—250°.

Reduction of 4-chloro-m-dinitrobenzene in almost neutral solution
yields a small amount of 2 : 2′(or 4 : 4′)-*dichloro*-5 : 5′-*dinitroazobenzene*,
m. p. 164°, together with a brown oil, containing 4- and 6-chloro-m-
nitrophenylhydroxylamines, which, however, could not be isolated from
the product, and were therefore identified by oxidation of the cathode
liquid with ferric chloride to the corresponding nitroso-compounds.

1-*Chloro-4-nitro-2-nitrosobenzene* forms white needles, m. p. 95°, and
has also been prepared by the oxidation of 6-chloro-m-nitroaniline with
Caro's acid.

1-*Chloro-2-nitro-4-nitrosobenzene*, prepared from 4-chloro-m-nitro-
aniline in a similar manner, forms white needles, m. p. 120°.

In neutral solution, 2 : 4-dinitroanisole is reduced at a silver cathode
to the above-mentioned 5 : 5′-dinitro-o-azoxyanisole and 5-*nitro-2-methoxy-
phenylhydroxylamine*, which forms a brownish-red, sandy, crystalline
powder, m. p. 129°, is reduced by copper powder and hydrochloric acid
to 4-nitro-o-anisidine, and on oxidation with ferric chloride yields a

compound, $C_{16}H_{16}O_8N_4$, m. p. 121°, the constitution of which has not yet been determined. F. B.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERICK S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, and JOHN T. HEWITT (*Rep. Brit. Assoc.*, 1912, 116—123).—See Orton and Jones, T, 1912, **101**, 1708, 1720.

C. H. D.

A Photochemical Reaction. FRÉDÉRIC REVERDIN (*Bull. Soc. chim.*, 1913, [IV], **13**, 485—486 *).—A solution of 3 : 5-dinitro 4-nitromethylaminotoluene in alcohol on exposure to sunlight slowly undergoes partial transformation into 3 : 5-dinitro-4-methylaminotoluene.

T. A. H.

Hexylenic Ethers. R. DIONNEAU (*Bull. Soc. chim.*, 1913, [iv], **13**, 519—525).—A more detailed account, with some new data, of work already recorded (A, 1910, i, 353). Phenoxyhexylene, D_4^0 0·9553, reacts with bromine in chloroform to give a *dibromide*, D_4^0 1·5415, b. p. 208°/35 mm. (decomp.), and with excess of hydriodic acid to form di-iodohexane, D_4^0 2·047, whilst with 1 mol. of the acid it gives iodophenoxyhexane, D_4^0 1·4385, b. p. 205°/33 mm., and a *substance*, D_4^0 1·516, b. p. 84°/33 mm. or 183°/760 mm., which may be iodohexylene. Iodophenoxyhexane through its magnesium derivative yields phenoxyhexane, from which Franchimont and Zincke's hexyl iodide is obtainable by heating with hydriodic acid; thus showing that in phenoxyhexylene the radicle C_6H_{11} is linear and carries the phenoxy-group on the first carbon atom. On oxidation with permanganate or ozone, phenoxyhexylene yields phenoxyvaleric and formic acids. These observations indicate that it has the formula $OPh\cdot[CH_2]_4\cdot CH{:}CH_2$.

Ethoxyhexylene (*loc. cit.*) has been prepared by the action of allyl iodide on the magnesium derivative of iodoethoxypropane.

T. A. H.

Aliphatic Dihalogen Compounds. JULIUS VON BRAUN (*Ber.*, 1913, **46**, 1782—1792).—A series of experiments is described on (1) the synthesis of brominated esters, (2) the preparation of polymethylene dibromides in which one $-CH_2-$ group is replaced by $-N(CN)-$, (3) ring-formations with sodium cyanamide, and (4) certain other ring-formations.

(1) Diprimary chloro-, bromo-, and iodo-compounds react readily with alkali phenoxides and alkoxides with the formation of halogenated ethers (for example, $Br[CH_2]_x\cdot OPh$), the use of which in synthetic operations is greatly limited by the difficulty of removing the phenoxy-radicle without completely decomposing the molecule. The author has, therefore, examined the halogen derivatives of alkyl carboxylates (compare A., 1909, i, 419) in this respect. When dry sodium benzoate (1 mol.) is heated with 1·5 mols. of various dibromides, the nature of the product formed depends greatly on the distance of the bromine atoms

from one another. Ethylene dibromide yields almost exclusively ethylene dibenzoate, bromoethyl benzoate, $CH_2Br\cdot CH_2\cdot O\cdot COPh$, not being detectable ; in the trimethylene series, the yield of brominated ester is 30%, in the tetramethylene series 45%, in the pentamethylene series above 60%, and in the heptamethylene series nearly 75%. These esters are readily saponifiable by acid or alkali, or even by protracted action of water and alcohol.

Trimethylene bromide and sodium benzoate yield trimethylene dibenzoate, m. p. 57°, and γ-bromopropyl benzoate, b. p. 162—164°/14 mm. When warmed with sodium iodide in alcoholic solution, the latter yields γ-iodopropyl benzoate, pale yellow oil, b. p. 175—178°/12 mm. δ-Bromobutyl benzoate, b. p. 176—178°/14 mm., together with tetramethylene dibenzoate, is similarly obtained from tetramethylene bromide. ε-Bromoamyl benzoate, b. p. 188—190°/12 mm., is most readily obtained from α : ε-dibromopentane and sodium benzoate at 200—210°. The corresponding pentamethylene dibenzoate is a liquid. ε-Bromoamyl benzoate is readily saponified by aqueous alcoholic potassium hydroxide with formation of pentamethylene oxide (compare Clarke, T , 1912, 101, 1802). η-Bromoheptyl benzoate is an oil, b. p. 205—210°/11 mm., which does not solidify. With sodium iodide it yields η-iodoheptyl benzoate, pale yellow oil, b. p. 220—224°/11 mm.

(2) The observation that in phenoxypropylbromoamylcyanamide (A., 1909, i, 507) the phenoxy-group is replaced by bromine more readily than the nitrile group is saponified under the action of hydrobromic acid has led the author to examine the possibility of introducing two phenoxy-alkyl residues into sodium cyanamide (compare Traube and Engelhardt, A., 1911, i, 955) with the ultimate object of replacing the phenoxy-groups by bromine,

$$N(CN)[(CH_2)_x OPh]_2 \longrightarrow N(CN)[(CH_2)_x Br]_2,$$

and thus obtaining polymethylene dibromides in which one –CH_2– group is replaced by $CN\cdot N<$.

γ-Phenoxypropyl iodide in alcoholic solution reacts readily with commercial sodium cyanide, yielding allyl phenyl ether and diphenoxypropylcyanamide, b. p. 295—300°/13 mm. The yield of the latter is nearly 60% of that theoretically possible. Fuming hydrobromic acid converts it into dibromopropylcyanamide, $CN\cdot N([CH_2]_3\cdot Br)_2$, a pale brown, heavy oil which is not volatile with steam, and cannot be distilled without decomposition. When dissolved in dry ether, it reacts readily with metallic sodium, yielding a product which is only partly volatile in a vacuum. The volatile portion, b. p. 110—120°/11 mm., was hydrolysed with hydrochloric acid, and identified as hexamethyleneimine ; the non-volatile portion was not identified. Phenoxyethyl bromide scarcely reacts with sodium cyanamide, but the corresponding iodide, m. p. 31—32°, yields phenylvinyl ether and diphenoxyethylcyanamide, white leaflets, m. p. 96°. In this compound the cyano- and phenoxy-groups are more simultaneously affected by hydrobromic acid than is the case with diphenoxypropylcyanamide, so that an approximately pure dibromide could only be obtained in small quantity. From β-iodoethyl ethyl ether, $I\cdot[CH_2]_2\cdot O\cdot C_2H_5$, and sodium cyanamide, the corresponding unsaturated ether is produced, whilst

ε-iodoamyl phenyl ether gives a product which is decomposed during distillation into amylene phenyl ether, CH_2·CH·$[CH_2]$,·O·Ph.

(3) When sodium cyanamide is boiled with an alcoholic solution of a : ε-pentamethylene dibromide, and the product treated with water, an oil is obtained which below 100°/12 mm. yields a small unsaturated fraction, at 110°/12 mm. gives a trace of 1-cyanopiperidino, and leaves a viscous, non-volatile oil. Similar results are obtained with a : ε-di-iodopentane and a : δ-di-iodobutane. From o-xylylene bromide and sodium cyanamide, a viscous product is obtained from which a small amount of a crystalline *product*, m. p. 235—236°, can be separated by methyl alcohol ; the substance appears to be a polymeride of cyanodihydroisoindole.

(4) a : η-Dibromoheptane forms with ethyl sodioacetoacetate an *oil*, which is decomposed on distillation, and on saponification yields β : μ-*diketotridecane*, $COMe$·$[CH_2]_9$·$COMe$, m. p. 72° (*semicarbazone*, m. p. 184°), together with nonanedicarboxylic acid and small quantities of the *keto-acid*, $COMe$·$[CH_2]_9$·CO_2H, m. p. 59—62°. The latter was not obtained in the pure state.

An attempt was made to synthesise suberone from a : δ-dibromo-butane and ethyl acetonedicarboxylate. The desired substance was only obtained in very small quantity.

Attempts were further made to form cyclic compounds containing mercury, by the action of sodium amalgam on a : δ-di-iodobutane and a : ε-di-iodopentane respectively. The substances obtained were only partly volatile in a vacuum, and probably consisted of polymerides of the substances required. H. W.

Amino-alcohols. Derivatives of Phenyl Glyceryl Ethers. P. BRENANS (*Bull. Soc. chim.*, 1913, [iv], 13, 525—535).—In continuation of the work of Fourneau (A., 1910, i, 246, 822), a number of new amino-alcohols of these types have been prepared with a view to the investigation of their therapeutic properties.

o-*Nitrophenoxypropanediol*, NO_2·C_6H_4·O·CH_2·$CH(OH)$·CH_2·OH, m. p. 45°, results from the action of monochlorohydrin on o-nitrophenol in presence of potassium hydroxide ; it crystallises in yellow spangles, and on reduction with tin and hydrochloric acid yields o-*aminophenoxypropanediol hydrochloride*, m. p. 170°, crystallising in silky needles ; the free *base* is very soluble in water. o-*Nitrophenyl glycide ether*,

$$NO_2\cdot C_6H_4\cdot O\cdot CH_2\cdot CH{<}^{CH_2}_{O},$$ m. p. 51—52°, formed by the action of

dichlorohydrin on o-nitrophenol in presence of alkali, crystallises in pale yellow needles. In this reaction some dinitrodiphenoxypropanol, m. p. 122° (compare Fourneau, *loc. cit.*), is formed.

p-*Nitrophenoxypropanediol*, m. p. 58°, prepared by the general method (above and *loc. cit.*), crystallises in slender, colourless needles, and on reduction furnishes the corresponding *amino*-compound, m. p. 133°, crystallising in ragged tablets and becoming brown in the light; the *hydrochloride*, m. p. 166°, forms colourless scales.

Tetranitrodiphenoxypropanol, OH·$CH[$·CH_2·O·$C_6H_3(NO_2)_2]_2$, m. p.

79°, obtained by the action of epichlorohydrin on the potassium derivative of 2:4-dinitrophenol, in presence of excess of alkali, or, better, on the silver derivative of the phenol, forms large, yellow-tinted crystals. On reduction with tin and hydrochloric acid, it yields the corresponding *tetra-amino*-compound *hydrochloride*, crystallising from methyl alcohol in small, yellow prisms and decomposing below 200° when heated.

o-*Nitro*-p-*tolyl glycide ether*, $NO_2 \cdot C_7H_6O \cdot CH_2 \cdot CH \underset{O}{\overset{CH_2}{<}}$, m. p.

66—67°, prepared by the action of dichlorohydrin on 2-nitro-p-cresol in presence of alkali, crystallises in bright yellow prisms. When heated with dimethylamine at 100° during ten hours, it yields *γ-dimethylamino-a-2-nitro-*p-*tolyloxypropanol*,

$$NO_2 \cdot C_7H_6O \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot NMe_2,$$

as a thick, yellow oil, giving a crystalline *benzoyl* derivative, m. p. 179°.

o-*Iodophenoxypropanediol*, m. p. 95°, prepared from o-iodophenol by the general method, crystallises in silky, colourless needles. o-*Iodophenyl glycide ether*, b. p. 200—202°/20 mm., is a colourless liquid, which, with dimethylamine, yields *γ-dimethylamino-a-o-iodophenoxypropanol*, b. p. 210°/20 mm. (decomp.), as a colourless syrup from which the *benzoylated hydrochloride*, m. p. 169—170°, may be obtained as slender, prismatic needles.

5-*Iodoguaiacyloxypropanediol*, $OMe \cdot C_6H_3I \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, m. p. 109°, crystallises in slender, colourless, odourless needles.

γ-Dimethylamino-a o-tolyloxypropanol, b. p. 175—178°/28 mm., gives a benzoyl derivative, the *hydrochloride* of which has m. p. 138° and crystallises in colourless, silky needles.

p-*Nitrobenzoyl-γ-dimethylamino-a-thymoxypropanol hydrochloride*, m. p. 161°, crystallises in large, yellow, octahedra from a mixture of alcohol and ether; the meta *isomeride*, m. p. 187°, forms small, hard prisms from alcohol.

m-*Tolyl glycide ether*, b. p. 136·5°/14 mm., on treatment with dimethylamine gives *γ-dimethylamino-a-*m-*tolyloxypropanol*, b. p. 178—180°/14 mm., as a colourless syrup; the *benzoylated hydrochloride*, m. p. 138—139°, crystallises in rectangular tablets from acetone.

T. A. H.

Preparation of Derivatives of Aldehydo- and Keto-cyano-hydrins containing Sulphur. August Albert (D.R.-P. 259502). —The crystalline *compound* (annexed formula), decomp. 145°, is obtained when a benzene solution of methylenedioxyacetylmandelo-nitrile, $CH_2 \overset{O}{\underset{O}{<}} C_6H_3 \cdot CH(CN) \cdot OAc$, is treated with alcoholic ammonia and the solution saturated at 0° with hydrogen sulphide; after some time the product separates in crystalline form.
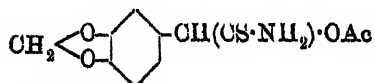
The *compound* from benzoyl-o-nitromandelonitrile crystallises with 1 mol. of ethyl alcohol and decomposes at 160°. F. M. G. M.

Chloroquinolsulphonic Acids and Their Conversion into Chloro-*p*-benzoquinonesulphonic Acids. ALPHONSE SEYEWETZ and J. PARIS (*Bull. Soc. chim.*, 1913, [iv], **13**, 486—491. Compare A., 1911, i, 360; this vol., i, 492).—Part of this work has been described already (*loc. cit.*). Chloroquinol on sulphonation by the method already described (*loc. cit.*) yields *sodium chloroquinolsulphonate*,

$$C_6H_2Cl(OH)_2 \cdot SO_3Na,$$
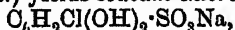
colourless leaflets, soluble in water, but not in alcohol, which acts as a photographic developer in presence of alkalis, and on oxidation by sodium dichromate and sulphuric acid yields *sodium chloro-*p-benzo-*quinonesulphonate*, bright yellow needles, soluble in water but not in alcohol, which has oxidising properties, and in aqueous solution liberates iodine from iodides in presence of acids. T. A. H.

Unsaturated Compounds. Method of Reaction of Enols and Phenols. KURT H. MEYER and S. LENHARDT (*Annalen*, 1913, **398**, 66—82).—It has been shown (this vol., i, 704) that the enolic grouping represents one of the most reactive states in organic chemistry. The additive capacity of the double linking is enormously increased by the presence of the hydroxyl group, as is proved by comparative experiments on the rate of addition, of alcoholic bromine and of *p*-nitro-benzenediazonium hydroxide, to pairs of substances differing only by the one containing a hydroxyl group where the other contains a hydrogen atom, as, for example, styryl methyl ketone and benzoyl-acetone. The reactivity of the enolic grouping is not connected, as Hinsberg supposes, with the dissociability of the hydrogen atom, because alkyl ethers of enols, which do not contain the mobile hydrogen atom, are also extremely reactive.

Recent researches on the action of ozone, potassium permanganate, and hydrogen on benzene have shown that the latter behaves like a substance containing very slowly reacting ethylenic linkings. The comparatively great reactivity of phenol, therefore, is explicable as being due to the activating influence of the hydroxyl group on the double linking. This view is supported by the fact that phenolic ethers are almost as reactive as phenol itself. Phenol, anisole, resorcinol, resorcinol dimethyl ether, α-naphthol, α-naphthyl methyl ether, β-naphthol, β-naphthyl methyl ether, and anthranol each reacts instantly with alcoholic bromine at 0°. The preceding ethers with the exception of anisole react as readily as phenol with diazo-hydroxides; *benzeneazophloroglucinol trimethyl ether*, m. p. 82·5°, garnet-red crystals, easily soluble in dilute mineral acids, p-*nitrobenzeneazophloroglucinol trimethyl ether*, m. p. 150·5°, brown needles with violet lustre, p-*nitrobenzeneazoresorcinyl dimethyl ether*, m. p. 152°, red needles, and p-*nitrobenzeneazo-α-naphthyl methyl ether*, m. p. 169°, red needles, are described. α-Naphthyl methyl ether in glacial acetic acid reacts readily with nitrous acid, yielding nitroso-α-naphthol, methyl alcohol being eliminated.

It is probable that all substances containing the groups ·CH:C·OR or ·CH:C·NR contain an activated ethylenic linking. Examples of the latter kind are found in the reactivity of pyrroles with aldehydes, halogens, and diazo-compounds; 1 : 2-dimethylindole condenses with

p-nitrobenzenediazonium hydroxide in glacial acetic acid to form a *substance*, $C_{10}H_{14}O_2N_4$, m. p. 204—205°, dark red crystals.   C. S.

Aromatic Telluretine Compounds. II. KARL LEDERER (*Ber.*, 1913, **46**, 1810—1812. Compare this vol., i, 615).—The methyl, ethyl, and propyl esters of α-bromopropionic acid have been heated to 50° with diphenyl telluride and the telluretine compounds isolated with difficulty and in poor yields. *Methyl diphenyl-α-propionyltelluretine bromide* [α-*bromodiphenyltelluripropionate*], $TePh_2Br \cdot CHMe \cdot CO_2Me$, and the *ethyl* and *propyl* esters, and also *methyl diphenyl-α-isobutyryltelluretine bromide* [α-*bromodiphenyltelluriisobutyrate*],

$$TePh_2Br \cdot CMe_2 \cdot CO_2Me,$$
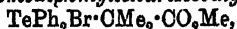
are white, amorphous substances with indefinite melting points.

J. C. W.

1-Benzoyl-2-phenyl-Δ²-*cyclo*pentene. ÉDOUARD BAUER (*Compt. rend.*, 1913, **156**, 1470—1472).—The conversion of αδ dibenzoylbutane into the two cyclic compounds 1-benzoyl-2-phenyl-Δ¹-and-Δ²-*cyclo*pentenes by the action of sodium ethoxide (compare A., 1912, i, 777) is equally well brought about by sodamide. 1-Benzoyl-2-phenyl-Δ²-*cyclo*pentene, thus constituted, should behave as a dialkylacetophenone (compare Haller and Bauer, A., 1909, i, 108), and the author has now proved this to be the case. It reacts with sodamide in anhydrous benzene, giving a sodium derivative which, on the addition of methyl iodide, is converted into the the corresponding 1-*benzoyl-2-phenyl-1-methyl-Δ²-cyclopentene* (formula II), b. p. 223—224°/23 mm., a viscid oil instantly decolorising potassium permanganate solution in the cold. This

(I.)   (II.)   (III.)   (IV.)
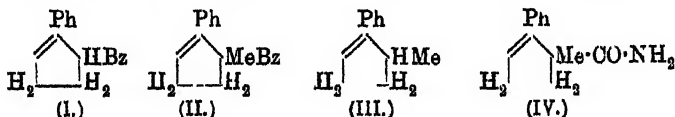
methyl derivative reacts further with sodamide (compare Haller and Bauer, *loc. cit.*) and is decomposed, giving a mixture of 2-*phenyl-1-methyl-Δ²-cyclopentene* (formula III), b. p. 116—117°/20 mm., and benzamide on the one hand, and benzene and 2-*phenyl-1-methyl-Δ²-cyclopentene-1-carboxylamide* (formula IV), m. p. 165°, on the other.

W. G.

1-Benzoyl-2-phenyl-Δ¹-*cyclo*pentene. ÉDOUARD BAUER (*Compt. rend.*, 1913, **156**, 1684—1686. Compare A., 1912, i, 777; preceding abstract).—Sodamide acts on 1-benzoyl-2-phenyl-Δ¹-*cyclo*pentene in the same manner as on benzophenone (compare A., 1908, i, 987), giving 2-phenyl-Δ¹-*cyclo*pentene-1-carboxylamide and benzene and 1-phenyl-Δ¹-*cyclo*pentene and benzamide.

On boiling 1-benzoyl-2-phenyl-Δ¹-*cyclo*pentene with sodamide in benzene a brick-red precipitate is obtained, which is decolorised on treatment with water. This product is separable by crystallisation from ether into benzamide and 2-*phenyl-Δ¹-cyclopentene-1-carboxylamide*, needles, m. p. 135—136°, which rapidly reduces alkaline permanganate

and decolorises bromine in chloroform. On hydrolysis with alcoholic potassium hydroxide it yields a mixture of two isomeric acids,

$$C_{12}H_{12}O_2,$$

separable by crystallisation from ether into 2-*phenyl*-Δ^1-*cyclopentene-carboxylic acid*, m. p. 157°, and an *acid*, m. p. 124—125°, differing from the other only in the position of the ethenoid linking in the nucleus, and which gives the corresponding *amide*, m. p. 178—179°.

From the original benzene solution, after distilling off the solvent, there is obtained 1-*phenyl*-Δ^1-*cyclopentene*, m. p. 23°, b. p. 120—121°/ 20 mm., D_1^{21} 0 98617, n_α^{21} 1·56723, n_D^{25} 1·5734, n_β^{21} 1·59017, which yields a *picrate*, m. p. 64·5°. On reduction by sodium in absolute alcohol it gives phenyl*cyclo*pentane. W. G.

Preparation of Nitriles from Thiocarbamides [and from Thiocarbimides]. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 259363, 259364).—It has been shown by Weith (A., 1875, 901, 908, 1241) that nitriles (in very small yield) can be obtained by the action of copper powder on thiocarbamides, and this reaction has now been carried out with cheaper material, such as iron, in the presence of machine or paraffin oils or anthracene.

o-Toluonitrile is obtained in 64% yield when a mixture of iron (20 parts) and paraffin (100 parts) is slowly treated at 280° with 10 parts of *o*-ditolylthiocarbamide. The preparation of the following compounds is also described : *m*-toluonitrile in 62% yield, *p*-toluonitrile in 75% yield, β-naphthonitrile in 75% yield, *m*-xylonitrile in 65% yield, *p*-methoxybenzonitrile in 67% yield, *p*-chlorobenzonitrile in 51% yield from *p*-dichlorophenylthiocarbamide, *p*-cyanoquinoline in 21% yield from *p*-diquinolylthiocarbamide, octonitrile in 61% yield from diheptylthiocarbamide, and phenylacetonitrile in 20% yield from dibenzylthiocarbamide.

The second patent describes the preparation of many of the preceding compounds by substituting the corresponding thiocarbimides for the thiocarbamides, the average yield of product being about the same. F. M. G. M.

Polymerisation. ABRAHAM KRONSTEIN (*Ber.*, 1913, **46**, 1812—1814).—A claim for priority in the study of polymerisation from the chemical, physical, technical, and also physiological points of view (compare Liebermann and Kardos, this vol., i, 476). J. C. W.

Preparation of Diphenyleneacetic Acid (9-Fluorenecarboxylic Acid) from Benzilic Acid and Aluminium Chloride. DANIEL VORLÄNDER and ALFRED PRITZSCHE (*Ber.*, 1913, **46**, 1793—1796).—The fact that Vorländer and Huth assumed the formation of the unknown nitrile of benzilic acid as an intermediate stage in the condensation of benzoyl cyanide to 9-cyanofluorene (A., 1911, i, 867) has led to the study of benzilic acid itself, with the result that a good method for the preparation of 9-fluorenecarboxylic acid has been discovered. Triphenylacetic acid could not be detected in the product, and therefore diphenylchloroacetic acid cannot represent an intermediate stage. Carbon disulphide, or preferably benzene, may be used as a solvent, but they do not enter into the reaction. The fluorene-

carboxylic acid was characterised by conversion into the unstable chloride with thionyl chloride, then into the *amide*,

$$\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!\!>\!\!CH\cdot CO\cdot NH_2,$$
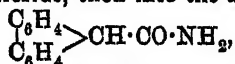
microscopic needles, m. p. 250°, and finally into the nitrile (Wislicenus and Russ, A., 1910, i, 840).

Phenylglyoxylic acid also condenses with benzene in presence of aluminium chloride, forming benzilic acid, and subsequently the above 9-fluorenecarboxylic acid. Ethyl phenylglyoxylate gives the same result, whereas the action of magnesium phenyl bromide leads to the formation of ethyl benzilate and, with an excess, benzopinacone. In toluene solution, phenylglyoxylic acid condenses to p-*methylfluorenecarboxylic acid*, $C_{15}H_{12}O_2$, which has m. p. 210°, and yields p-*methylfluorene* in leaflets, m. p. 88°, on distillation with soda-lime.

The alkaline solution of the condensation product of diphenylene-glycollic acid and benzene has a violet fluorescence and contains a little 9-*phenylfluorenecarboxylic acid*, $C_{20}H_{14}O_2$, which crystallises in white needles, m. p. 183°, and is easily transformed into 9-phenylfluorene (Kliegl, A., 1905, i, 187). J. C. W.

Pimaric Acid. LEO A. TSCHUGAEV and P. TEEARU (*Ber.*, 1913, 46, 1769—1774. Compare Vesterberg, A., 1886, 365, 1038; 1888, 249; 1906, i, 92; 1907, i, 213).—The authors confirm Vesterberg's conclusion that galipot must contain at least three acids. *d*-Pimaric acid has m. p. 211—212°, $[\alpha]_C + 55\cdot40°$, $[\alpha]_D + 72\cdot52°$, $[\alpha]_E + 97\cdot20°$, $[\alpha]_F^- + 123\cdot0°$, $[\alpha]_F/[\alpha]_C$ 2·20°. 2·129 Grams of acid are soluble in 100 grams of absolute methyl alcohol at 25°. The acid is monobasic. The sodium salt has $[\alpha]_C + 30\cdot12°$, $[\alpha]_D + 38\cdot86°$, $[\alpha]_E + 52\cdot42°$, $[\alpha]_F + 67\cdot37°$, $[\alpha]_F/[\alpha]_C$ 2·23° in methyl-alcoholic solution ($c = 2\cdot174$). Methyl pimarate, m. p. 69°, obtained by the action of methyl sulphate on an aqueous alcoholic solution of sodium pimarate in the presence of an excess of sodium hydroxide or carbonate, has $[\alpha]_C + 46\cdot30°$, $[\alpha]_D + 60\cdot45°$, $[\alpha]_E + 81\cdot36°$, $[\alpha]_F + 102\cdot7°$, $[\alpha]_F/[\alpha]_C$ 2·22.

In the presence of spongy platinum, hydrogen converts *d*-pimaric acid into *dihydropimaric acid*, m. p. 240—241°; 100 grams of absolute methyl alcohol dissolve 0·478 gram acid. In ethyl alcoholic solution ($c = 0\cdot566$) at 20° the latter has $[\alpha]_C + 14\cdot57°$, $[\alpha]_D + 19\cdot43°$, $[\alpha]_E + 26\cdot05°$, $[\alpha]_F + 37\cdot53°$, $[\alpha]_F/[\alpha]_C$ 2·57. It is monobasic, and forms salts closely resembling those of pimaric acid. The *sodium* salt has in methyl alcoholic solution ($c = 3\cdot568$) at 20°, $[\alpha]_C + 4\cdot41°$, $[\alpha]_D + 5\cdot46°$, $[\alpha]_E + 7\cdot84°$, $[\alpha]_F + 11\cdot14°$, $[\alpha]_F/[\alpha]_C$ 2·56. The *ammonium* salt crystallises in long, thin needles.

The authors consider that pimaric acid is probably a tetracyclic compound with one double bond. H. W.

Preparation of Phenolcarboxylic Acids. JOSEPH ZELTNER and MAX LANDAU (D.R.-P. 258887. Compare A., 1876, ii, 632; 1877, i, 77; ii, 415).—The action of chloroform or carbon tetrachloride on phenols has been studied (*loc. cit.*), and the reaction is now found to proceed smoothly under atmospheric pressure in the presence of copper powder, or a salt of copper.

When phenol (9·4 parts), a 40% solution containing potassium hydroxide (39·2 parts), carbon tetrachloride (16 parts), and 0·3 part of copper, are boiled together during eight hours under reflux, it gives rise to a mixture of salicylic acid (25%) and *p*-hydroxybenzoic acid (30%).

The preparation of the following compounds is also described: 4-hydroxy-*m*-toluic acid, m. p. 146—147°, in 60% yield from *p*-cresol; an 80—80% yield of a mixture of 6- and 4-hydroxy-*m*-toluic acids from *o*-cresol. A 45% yield of 3-nitrosalicylic acid (compare Hasse, *loc. cit.*) from *o*-nitrophenol; and of 5-chlorosalicylic acid (in 75% yield) from *p*-chlorophenol. Guaiacol furnished vanillic acid, m. p. 207°, and quinol gave rise to gentisic acid. Salicylic acid gave a 70—75° yield of a mixture of phenol-2 : 4· and 2 : 6-dicarboxylic acids separable by means of their barium salts, whilst *m*-cresotic acid furnished *a*-coccinic acid (A., 1897, i, 539), and *o*-cresotic acid yielded 1-hydroxy-2-methyl-benzene-4 : 6-dicarboxylic acid (*a*-hydroxyuvitic acid), m. p. 294—295°.

F. M. G. M.

Preparation of Acetylcarbinyl *o*-Thymotate. ADOLF DIEFEN-BACH and RICHARD ZAHN (D.R.-P. 258936).—The methyl and ethyl esters of *o*-thymotic acid are known (A., 1910, i, 38), and *acetylcarbinyl o-thymotate*, m. p. 75° (annexed formula), has now been prepared by the action of monochloroacetone on sodium *o*-thymotate.

$$CH_3$$
$$CO_2 \cdot CH_2Ac$$
$$OH$$
$$C_3H_7$$

F. M. G. M.

a-Hydroxy-γ-phenylcrotonic Acid; its Preparation; New Isomerisation. J. BOUGAULT (*Compt. rend.*, 1913, 156, 1468—1470. Compare A., 1912, i, 770; this vol., i, 269).—*a*-Hydroxy-γ-phenylcrotonic acid is most readily prepared from its amide by choice of suitable hydrolysing agents, which will not bring about its isomerisation into benzylpyruvic or benzoylpropionic acids. Aqueous solutions of alkali carbonates or hydrogen carbonates boiled for thirty to forty minutes with the amide convert 30—40% into the acid required, with only a small admixture of its isomerides. As acid hydrolysing agents, the best are aqueous solutions of oxalic or phosphoric acids, oxalic acid (7½%) giving a yield of 80% of the acid required.

The author has isolated a new isomeride, m. p. 91°, which appears to be the *enolic* form of benzoylpropionic acid, and to have the constitution $C_6H_5 \cdot C(OH){:}CH \cdot CH_2 \cdot CO_2H$. It is readily converted by alkalis and strong acids into the ketonic form.   W. G.

Preparation of Halogen Alkyl Esters of *o*-Acetoxybenzoic Acid. RICHARD WOLFFENSTEIN (D.R. P. 258888. Compare A., 1912, i, 556, 768).—The crystalline *ester*, $OAc \cdot C_6H_4 \cdot CO \cdot O \cdot CHMe \cdot CCl_3$, m. p. 52°, is obtained when *o*-acetoxybenzoyl chloride is heated with trichloro*iso*propyl alcohol in the presence of dimethylaniline, whilst the tribromo-*tert.*-butyl *o*-acetoxybenzoate, m. p. 90°, is prepared by the action of *o*-acetoxybenzoyl chloride on acetonebromoform [tribromo-*tert.*-butyl alcohol], $OH \cdot CMe_2 \cdot CBr_3$, and the *compound* formed when the latter constituent is replaced by dichloro*iso*butyl alcohol is also mentioned.   F. M. G. M.

Benzoylcyanohydrins of Ketones, and Amides, and Hydroxy-acids Derived from Them. JULES ALOY and CHARLES RABAUT (*Compt. rend.*, 1913, **156**, 1547—1549. Compare A., 1912, i, 462).— Benzoylcyanohydrins can be readily obtained from ketones by the gradual addition of benzoyl chloride (1/10th mol.) to a solution of potassium cyanide (1/10th mol.) in 100 c.c. of water containing the ketone (1/10th mol.). The mixture is shaken for three hours and then extracted with ether, from which the cyanohydrin crystallises. They are, in general, quite crystalline and stable, and are hydrolysed by sulphuric acid, giving the corresponding benzoylamide, which is further hydrolysed by sodium hydroxide to benzoic acid and the hydroxy-acid.

Thus acetone gives *propylidenebenzoylcyanohydrin*, OBz·CMe₂·CN, m. p. 36—37°, yielding the *amide*, OBz·CMe₂·CO·NH₂, m. p. 142—143°, which is hydrolysed to α-*hydroxy-α-methylpropionic acid*, m. p. 79°.

Methyl propyl ketone yields β-*amylidenebenzoylcyanohydrin*, a syrupy liquid, hydrolysing to the *benzoylamide*, m. p. 126°, which on further hydrolysis yields α-*hydroxy-α-methylvaleric acid*, OH·CPrMe·CO₂H, m. p. 46—47°.

Diethyl ketone gives a small yield of γ-*amylidenebenzoylcyanohydrin*, a liquid, which furnishes an *amide*, OBz·CEt₂·CO·NH₂, m. p. 149—150°.

*cyclo*Hexanone gives *cyclohexylidenebenzoylcyanohydrin*,

$$OBz·C_6H_{10}·CN,$$
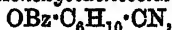
m. p. 71°, yielding an *amide*, m. p. 118°, which is hydrolysed to *cyclo*hexanol-1-carboxylic acid.

3-Methyl*cyclo*hexanone gives a *benzoylcyanohydrin*, m. p. 125—126°, yielding the *amide*, m. p. 135—136°, which on hydrolysis gives 3-methyl*cyclo*hexanol-1-carboxylic acid.

4-Methyl*cyclo*hexanone is converted into the *benzoylcyanohydrin*, m. p. 86°, this giving an *amide*, m. p. 122°, which finally yields 4-*methyl*cyclohexanol-1-*carboxylic acid*, m. p. 80—81°.   W. G.

The Action of Nitric Acid on the Dihydroxybenzoic Acids. FRANZ VON HEMMELMAYR (*Monatsh.*, 1913, **34**, 811—820).—Of the dihydroxybenzoic acids it is not the compound in which the carboxyl group is most firmly attached which can be nitrated most satisfactorily, but the important condition apparently is resistance to oxidation by the nitric acid ; for example, β-resorcylic acid can be nitrated successfully, whilst gentisic acid, the nitro-derivative of which is much more stable, is for the greater part oxidised to oxalic acid. The author has therefore compared the behaviour of these acids towards nitric acid (D 1·4), and finds that the acids derived from catechol and quinol are oxidised almost entirely to oxalic acid. It is an interesting fact that those acids in which the meta-positions are unoccupied and in which at least one of these vacant positions is in a para-position to a hydroxy-group, more readily undergo nitration (compare von Hemmelmayr, this vol., i, 468).

3 : 4-Dihydroxybenzoic (protocatechuic) acid with the nitric acid alone or in acetic acid solution gave much oxalic acid, together with orange-red needles of a *substance*, $C_6O_{10}N_4$, possibly tetranitro-o-benzoquinone.

2 : 3-Dihydroxybenzoic acid gave a vigorous reaction with production of oxalic acid.

3 : 5-Dihydroxybenzoic (α-resorcylic) acid reacted vigorously, giving mainly oxalic acid together with a small quantity of an impure yellow, crystalline *substance*. By allowing the nitration to proceed in ethereal solution, the oxidising effect of nitric acid is diminished, and a *nitro-3 : 5-dihydroxybenzoic* acid, deep red needles, m. p. 210° (decomp.), could be isolated in small quantity.

2 : 6-Dihydroxybenzoic (γ-resorcylic) acid gave a vigorous reaction from the product of which a *trinitrohydroxybenzoic acid*, brownish-red, microscopic needles, decomp. at 240°, could be isolated.

2 : 5-Dihydroxybenzoic (gentisic) acid, when nitrated in cold ethereal solution, gave an approximately 30% yield of nitrogentisic acid (compare Klemenc, this vol., i, 49), which crystallises with $2H_2O$.

<div align="right">D. F. T.</div>

Preparation of Anthraquinone-α-carboxylic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 259365. Compare A., 1911, i, 279 ; 1912, i, 979 ; this vol., i, 49).—1-*Chloroanthraquinone-4-carboxylic acid*, m. p. 229—230°, is prepared by heating together phthalic anhydride and p-chlorotoluene in nitrobenzene solution, and introducing chlorine at a temperature of 160—170°.

When phthalic anhydride and m-xylene are condensed in the presence of chlorine, they furnish 3-methylanthraquinone-1-carboxylic acid, m. p. 246—247°, and apparently identical with that previously prepared by Wachendorff and Zincke (A., 1878, 232), whilst oxidation of the sodium salt with potassium permanganate furnishes *anthraquinone-1 : 3-dicarboxylic acid*, m. p. above 300°. F. M. G. M.

Preparation of Phenylmethylphthalide. ALFONS OSTERSETZER (*Monatsh.*, 1913, 34, 795—796).—From analogy to the behaviour of the o-aldehydic acids which yield alkyl substituted phthalides (Mermod and Simonis, 1908, i, 342 ; Simonis, Marben and Mermod, 1906, i, 32), it might be expected that o-ketonic acids when treated with a Grignard reagent should yield dialkyl substituted phthalides.

The reaction product of o-benzoylbenzoic acid and magnesium phenyl bromide is an oil, but magnesium methyl iodide gave phenylmethyl-phthalide, $C_6H_4{<}^{CMePh}_{CO}{>}O$, leaflets, m. p. 76°; the intermediate hydroxy-acid could not be isolated.

<div align="right">D. F. T.</div>

The Action of Phthalylacyl Chlorides on Benzene and Aluminium Chloride. ERNST PFAEHLER (*Ber.*, 1913, 46, 1700—1702).—Although phthalylphenylglycyl chloride (Pfaehler, this vol., i, 751) behaves similarly to phthalylglycyl chloride and the aliphatic homologues of this substance towards benzene and aluminium chloride, some of its higher homologues, such as phthaliminophenyl-propionyl chloride, act in a different manner.

Phthaliminophenylpropionyl chloride,

$$C_6H_4{<}^{CO}_{CO}{>}N{\cdot}CH(CH_2Ph){\cdot}COCl,$$
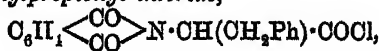
m. p. 131—132°, was obtained from the corresponding *acid*, m. p. 176—177°, which is produced when phthalaminobenzylmalonic acid, m.p. 160—170° (compare Sörensen, A., 1903, i, 834), is heated. When warmed with an equimolecular quantity of aluminium chloride in benzene solution, 2-phthalimino-1-hydrindone,

$$C_6H_4{<}^{CO}_{CO}{>}N{\cdot}CH{<}^{CH_2}_{CO}{>}C_6H_4,$$
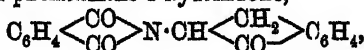
m. p. 191°, is obtained by intramolecular elimination of hydrogen chloride; it was not found possible to produce this substance by direct dehydration of the free acid. By heating the phthaliminohydrindone in acetic acid solution with fuming nitric acid at first in the open and afterwards in a sealed tube at 135°, the phthalyl nucleus is oxidised with the production of 2-amino 1-hydrindone hydrochloride,

$$C_6H_4{<}^{CH_2}_{CO}{>}CH{\cdot}NH_2,HCl$$
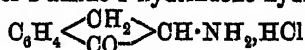
(compare Gabriel and Stelzner, A., 1897, i, 61).   D. F. T.

Hydrogenation of Santonic Acid. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 507—510).—When sodium santonate is treated with hydrogen in presence of platinum-black until no more gas is absorbed, a *tetrahydrosantonic acid*, $C_{15}H_{24}O_4$, is formed; it crystallises in prisms or in leaflets, m. p. 190° (decomp.). The same tetrahydro-derivative was obtained in an experiment in which only one-fourth of the requisite amount of hydrogen was employed, and a corresponding quantity of santonate remained unaltered. In this experiment was also isolated a small quantity of a *substance*, which formed acicular prisms, m. p. about 99°, and gave a green fluorescence with alcoholic potassium hydroxide. This compound of m. p. 99° gives an *oxime*, which crystallises in lustrous needles, m. p. about 235°. Tetrahydrosantonic acid dissolves in carbonates in the cold, gives no coloration with alcoholic potassium hydroxide, and has no bitter taste. When treated with acids it loses water. It dissolves readily in concentrated hydrochloric acid; the solution becomes greenish-brown, and if left exposed to the air deposits a *substance*, which after recrystallisation forms large, colourless, prismatic crystals, m. p. 88°. This compound does not dissolve in carbonates in the cold, but when its alkaline solution (obtained in the warm) is acidified, an *acid* separates in laminar crystals, which at first have m. p. about 130°, but after exposure to the air acquire the m. p. of tetrahydrosantonic acid. The substance of m. p. 88° crystallises from light petroleum in laminæ or in prisms of m. p. 102°, and these are converted into tetrahydrosantonic acid by boiling with potassium hydroxide. Conversely, if tetrahydrosantonic acid is boiled with *N*-sulphuric acid the substance of m. p. 102° is obtained. Tetrahydrosantonic acid yields an *oxime*, which crystallises in colourless prisms, m. p. 222° (decomp.), and on boiling with dilute sulphuric acid yields the above-mentioned compound of m. p. 102°. When an acetic acid solution of the oxime is treated with nitrous acid, a crystalline *compound* of m. p. 130° is formed; it yields a blue coloration with a sulphuric acid solution of diphenylamine. On treatment with concentrated sulphuric acid the oxime is converted into a *substance* which crystallises in rectangular tablets,

m. p. 235° (not sharply); this compound does not dissolve in carbonates in the cold, and it reduces Fehling solution after hydrolysis with acid. The two oximes which have been mentioned can be obtained directly from the raw product of the hydrogenation, but together with them there is then observed a third *oxime*, which forms small, colourless needles, m. p. 240° (decomp.). From alkali solutions of this substance sulphuric acid precipitates a *compound*, crystallising in regular, hexagonal laminæ, m. p. 160—162°. R. V. S.

Hydrogenation of Santonin. YASUHIKO ASAHINA (*Ber.*, 1913, **46**, 1775—1777).—*Tetrahydrosantonin*, $C_{15}H_{22}O_3$, is formed by the action of hydrogen on a solution of santonin in glacial acetic acid in the presence of platinum-black. It consists of thin, white leaflets, m. p. 155—156°, $[a]_D^{23}$ +60·56°, in chloroform solution. It yields a clear solution after protracted boiling with saturated aqueous barium hydroxide, from which the original substance is reprecipitated on acidification, and thus contains the lactonic group intact. In glacial acetic acid solution, it is stable towards permanganate. It yields an *oxime*, $C_{15}H_{23}NO_3$, m. p. 225°, $[a]_D^{20}$ −17·78°, in chloroform solution.

The author is led to the conclusion that the annexed formula for santonin most readily harmonises with the above data. H. W.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. IX. Derivatives of Pyrogallolcarboxylic Acid. EMIL FISCHER and MAX RAPAPORT (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 493—506).—When an excess of methyl chloro-formate is allowed to act on pyrogallolcarboxylic acid the trimethylcarbonato-compound is obtained. Phosphorus pentachloride converts it into the corresponding chloride, which crystallises from ether and has been used for the following synthetic operations.

Benzene and aluminium chloride convert it into a product yielding 2 : 3 : 4-trihydroxybenzophenone on hydrolysis, which is identical with the dye alizarin-yellow-A; the structure of this is thus established.

By interaction of the chloride in alkaline solution with *p*-hydroxybenzoic acid and subsequent elimination of the methylcarbonato-groups the didepside, *pyrogallolcarboyl-p-hydroxybenzoic acid*,

$$C_6H_2(OH)_3 \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H,$$
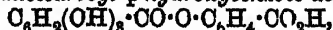
isomeric with galloyl-*p*-hydroxybenzoic acid is obtained.

The new term, carboyl, denoting the carboxylic acid radicle is derived in a similar way to benzoyl from benzoic acid—the radicle of pyrogallolcarboxylic acid is thus pyrogallolcarboyl.

When dextrose is shaken with the chloride and quinoline in chloroform solution, five trimethylcarbonatopyrogallolcarboyl residues are introduced into the sugar. On cautious hydrolysis a tannin is obtained isomeric with pentagalloyldextrose.

Trimethylcarbonatopyrogallolcarboxylic acid, $C_6H_2(O \cdot CO_2Me)_3 \cdot CO_2H,$

crystallises in tiny, colourless platelets, m. p. 122—124° (corr.). The pure acid gives hardly any coloration with ferric chloride.

The corresponding *chloride* crystallises in colourless, lancet-shaped needles, m. p. 67—68° (corr.).

The *methyl* ester, $C_6H_4(O \cdot CO_2Me)_3 \cdot CO_2Me$, crystallises in microscopic, stout double pyramids, m. p. 82—84°, the homologous *ethyl* ester crystallises in tiny, oblique plates, m. p. 91—94° (corr.).

Trimethylcarbonatopyrogallolcarboyloxybenzoic acid,
$$C_6H_2(O \cdot CO_2Me)_3 \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H,$$
crystallises in slender, microscopic platelets, m. p. 198—199° (corr.). Ammonia converts it into *pyrogallolcarboyl-p-hydroxybenzoic acid*, $C_6H_2(OH)_3 \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H$. The didepside crystallises in very small, lustrous crystals aggregated in bunches, m. p. 235—238° (corr., decomp.). With ferric chloride a blue or bluish-violet coloration is produced.

Penta-[trimethylcarbonatopyrogallolcarboyl]-dextrose,
$$C_6H_7O_6[CO \cdot C_6H_2(O \cdot CO_2Me)_3]_5,$$
forms a colourless, amorphous powder which sinters at 100°, m. p. about 130°, $[\alpha]_D^{18}$ +27°.

Pentapyrogallolcarboylglucose forms also a colourless, amorphous powder, which sinters about 160°, m. p. 200° (decomp.), $[\alpha]_D^{18}$ +69·1°. It differs from tannic acid and pentagalloylglucose in being sparingly soluble in water.   E. F. A.

Synthesis of *o*-Diorsellinic Acid. EMIL FISCHER and HERMANN O. L. FISCHER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 507—512).— Two didepsides are derived from orsellinic acid according as coupling takes place in the ortho- or para-positions. The product previously obtained (this vol., i, 477), identical with the natural lecanorcic acid, was considered to be the *p*-diorsellinic acid, and this is now confirmed by the synthesis of the ortho-isomeride.

Methylcarbonato-orcylaldehyde (Hoesch, this vol., i, 474) is readily coupled with dimethylcarbonato-orsellinyl chloride in alkaline solution, yielding the following compound (I). The corresponding acid is
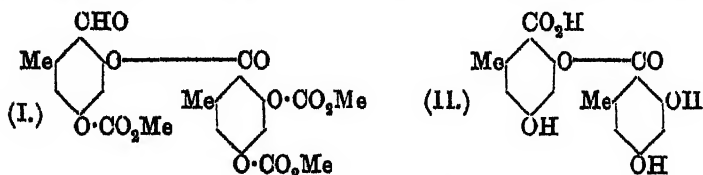
obtained on oxidation with permanganate, and it is converted into the *o*-diorsellinic acid on elimination of the methyl carbonato-groups by means of dilute ammonia. The *o*-diorsellinic acid (II) differs from lecanoric acid in solubility, melting point, and in its behaviour towards ferric chloride. It differs also from the gyrophoric acid described by Hesse (A., 1901, i, 151).

Trimethylcarbonato-orsellinoylorcylaldehyde crystallises in slender, pliable needles, m. p. 112—113° (corr.).

Trimethylcarbonato o-diorsellinic acid separates in tiny, six-sided

platelets which sinter at 150°, m. p. 158° (corr., decomp.). With ferric chloride only a yellow coloration is obtained.

o-*Diorsellinic acid* (formula II) forms colourless, tiny needles much intergrown, but appears somewhat yellow in bulk. It has m. p. 120—125°, becomes solid, and melts again at 180—185°. E. F. A.

Angeli-Rimini Reaction of the Aldehydes. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 575—579).—Polemical. A reply to Angeli (A., 1912, i, 626). R. V. S.

Quantitative Investigation of the Photochemical Transformation of o-Nitrobenzaldehyde into o-Nitrosobenzoic Acid. ANTON KAILAN (*Ber.*, 1913, 46, 1628—1634) —Polemical. The author maintains the sufficiency of his methods and the accuracy of the results obtained by him (this vol., i, 51) against the criticism of Weigert and Kummerer (this vol., ii, 370). R. V. S.

Some Derivatives of Methyl*cyclo*pentan-3-one. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1913, 156, 1779—1781. Compare this vol., i, 278).—By the action of dry chlorine on methyl-*cyclo*pentan-3-one in diffused light at a temperature below 25°, 2-*chloro-methyl*cyclopentan-3-one, C_6H_9OCl, is obtained as a colourless oil, b. p. 80—82°/8 mm., D^{22} 1·128, n_D^{22} 1·465. On boiling this chloro-derivative with water it yields a mixture of *methyl*cyclopentan-2-ol-3-one, b. p. 83—85°/12 mm., and 2-*methyl*-Δ^1-cyclopenten-5-one, b. p. 50°/12 mm. The former of these compounds is a pale yellow, syrupy liquid, giving a violet coloration with ferric chloride, and yielding an unstable *phenyl-hydrazone*. On oxidation the ketone-alcohol is converted into a-methyl-glutaric acid. 2-Methyl-Δ^1-cyclopenten-5-one is a colourless liquid, having b. p. 157—158°, D^{-6} 0·9712, n_D^{26} 1·4714. It is very soluble in water, and gives a *semicarbazone*, m. p. 230°, and an *oxime*, m. p. 127°. W. G.

Reduction of Ketones and Aldehydes to the Corresponding Hydrocarbons by means of Amalgamated Zinc and Hydrochloric Acid. ERIK CLEMMENSEN (*Ber.*, 1913, 46, 1837—1843).—The application of amalgamated zinc has led to very good results in the reduction of fatty-aromatic ketones, and of aliphatic ketones and aldehydes to the corresponding hydrocarbons. In practice, an excess of granulated zinc is left for an hour with 5% mercuric chloride, drained, and then heated with the substance and concentrated hydrochloric acid under reflux, care being taken that the evolution of hydrogen is brisk enough to keep the two liquids well mixed.

By this means acetophenone gives ethylbenzene, or by using only the theoretical amount of acid, styrene. Propiophenone or phenyl-acetone give 90% yields of *n*-propylbenzene; butyrophenone or benzyl-acetone give 88—100% yields of *n*-butylbenzene, and methyl a-naphthyl ketone is reduced to a-ethylnaphthalene. Aromatic aldehydes are too susceptible to the action of mineral acids, but, notwithstanding, a 46%

yield of toluene was obtained from benzaldehyde. Heptaldehyde, however, gives a good yield of *n*-heptane. The following reductions of aliphatic ketones give almost theoretical yields; methyl *n*-nonyl ketone to *n*-undecane, methyl *n*-heptadecyl ketone to *n*-nonadecane, di-*n*-heptadecyl ketone (stearone) to *n*-pentatriacontane. The method is being extended to other classes of compounds.   J. C. W.

Dynamic Isomerism. HENRY E. ARMSTRONG, THOMAS M. LOWRY, SIDNEY YOUNG, CECIL H. DESCH, JAMES J. DOBBIE, MARTIN O. FORSTER, and ARTHUR LAPWORTH (*Rep. Brit. Assoc.*, 1912, 115—116).—See Lowry and Glover, T., 1913, **103**, 913.   C. H. D.

Synthesis of Violanthrone. CHRISTIAN SEER and ROLAND SCHOLL (*Annalen*, 1913, **398**, 82—96).—The constitution of violanthrone has been now proved, since the orientation of the benzoyl groups in the dibenzoyl-*aa*-dinaphthyl used in its synthesis (this vol., i, 59) has now been definitely settled.

aa-Naphthidine in 3% hydrochloric acid at 0° is treated with sodium nitrite, and the tetrazotised solution is filtered into aqueous potassium cyanide and copper sulphate at 60°, whereby 4 : 4′ *dicyano-a : a′-dinaphthyl*, m. p. 280—281°, pale yellow needles, is obtained. The latter is hydrolysed by alcoholic sodium hydroxide at 160—190°, and the resulting *aa-dinaphthyl-4 : 4′-dicarboxylic acid*, m. p. 349—350°, colourless crystals, is converted by phosphoric and phosphoryl chlorides into the acid *dichloride*, pale brown crystals, from which 4 : 4′-dibenzoyl-*aa*-dinaphthyl is obtained by means of aluminium chloride and benzene in nitrobenzene at 70—75°. 4 : 4′-Dibenzoyl-*aa*-dinaphthyl has now been prepared in orange-yellow needles, m. p. 146—147°; it is converted into violanthrone by aluminium chloride at 95—100° (*loc. cit.*).

By treatment with hydriodic acid, b. p. 127°, and red phosphorus at 190° for ten hours, violanthrone is converted into a substance which is apparently its parent hydrocarbon, *violanthrene*, $C_{34}H_{20}$; it is a dark powder which is not attacked by alkaline sodium hyposulphite, and forms in concentrated sulphuric acid a blue solution with a brown fluorescence.

5-*Iodo*-1-*naphthoic acid*, m. p. 253—254°, colourless needles, prepared in the usual manner from 5-amino-1-naphthoic acid, forms a *methyl* ester, $C_{12}H_9O_2I$, m. p. 81—82°. By heating the latter with copper powder at 220—240° in a current of carbon dioxide, *methyl aa-dinaphthyl-5 : 5′-dicarboxylate*, $C_{24}H_{18}O_4$, m. p. 173—174°, faintly yellow needles, is obtained. The *acid*, $C_{22}H_{14}O_4$, m. p. 359—360°, microscopic needles, is converted into the crude *chloride*, m. p. about 150°, by phosphorus pentachloride, and the chloride is heated with aluminium chloride, benzene, and nitrobenzene at 70—80°, whereby 5 : 5′-*dibenzoyl-aa-dinaphthyl*, $C_{34}H_{22}O_2$, m. p. 248—250°, glistening leaflets, is obtained. By heating the latter with aluminium chloride at 145°, neither *Bz*-1 : 1′-dibenzanthronyl nor violanthrone is produced, but benzanthrone ; whether this is present as such in the crude 5 : 5′-dibenzoyl-*aa*′-dinaphthyl or is produced during the reaction was not determined.   C. S.

Conversion of 3-Dimethylaminophenyl Methyl Sulphide into 3-Methylthiol p-benzoquinone. THEODOR ZINCKE and JOHANNES MULLER (*Ber.*, 1913, **46**, 1777—1781. Compare this vol., i, 355).—3-*Methylthiol*-4 *nitrosodimethylaniline hydrochloride* separates in red needles when a solution of sodium nitrite is added to a well-cooled solution of 3-dimethylaminophenyl methyl sulphide in hydrochloric acid. The free *base* is best obtained by addition of sodium acetate, and forms green needles melting at 143° to a deep blue liquid. When boiled with *N*-sodium hydroxide, it yields dimethylamine and 4-*nitroso*-3-*methylthiolphenol*, yellow needles, m. p. 186°, which is converted by acetic anhydride and sodium acetate into the corresponding *acetyl* derivatives, yellow needles, m. p. 165°. 4-*Amino*-3-*methylthiolphenol* is obtained by reduction of a boiling ammoniacal solution of 4-nitroso-3-methylthiolphenol by hydrogen sulphide, and, after purification by sublimation in a vacuum, forms nearly colourless needles, m. p. 154°, which readily oxidise on exposure to air. The *alkali* salts and the *hydrochloride* are readily soluble; the *sulphate* is more sparingly soluble. The *diacetyl* derivative forms small, white crystals, m. p. 100°, which contain ½ mol. acetic acid. When warmed with salicylaldehyde in alcoholic solution, the free base yields a *substance*,

$$C_{14}H_{13}O_2NS,$$

yellowish-brown needles, m. p. 134°.
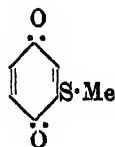
3 *Methylthiol* - p - *benzoquinone* (annexed formula) is obtained by addition of dichromate solution to a solution of 4-amino-3-methylthiolphenol in dilute sulphuric acid and subsequent oxidation of the bluish-black *product* so obtained with nitric acid in acetic acid solution. An excess of nitric acid causes the elimination of the methylthiol group. It is therefore preferable to reduce the above quinhydrone to the quinol and oxidise the latter with dilute sulphuric acid and dichromate solution. 3-Methylthiol-p-benzoquinone forms red needles, m. p. 148°. Concentrated nitric acid (D 1·4) dissolves it without change; sulphurous acid reduces it to the corresponding quinol. When dissolved in chloroform and treated with chlorine, it gives tetrachloro-p-benzoquinone, whilst with aniline in hot glacial acetic acid solution it yields 2 : 5-dianilino-p-benzoquinone and methyl mercaptan.

3-*Methylthiolquinol* forms white needles, m. p. 83°, which are readily oxidised on exposure to air. With acetic anhydride and sodium acetate it yields a *diacetyl* compound, m. p. 101°.　H. W.

2-Aminoanthraquinone. FRITZ ULLMANN and ROBERT MEDENWALD (*Ber.*, 1913, **46**, 1798—1809).—Two iminoanthraquinone nuclei have been linked together by an ethylene group, the sulphonic acid derived from aminoanthraquinone has been shown to be the 3-sulphonic acid, the preparation of the 1-nitro- and 3-nitro-2-aminoanthraquinones is described, and the condensation of 1 : 3-dibromo-2-aminoanthraquinone with bases has been studied.

Toluene-p-*sulpho* - 2 - *anthraquinonylamide*, $C_{14}H_7O_2 \cdot NH \cdot SO_2 \cdot C_7H_7$, from 2-aminoanthraquinone and p-toluenesulphonyl chloride in pyridine,

forms yellow needles, m. p. 304° (corr.), which give a red solution in hot alkalis or cold concentrated sulphuric acid. Excess of the sulphonyl chloride gives rise to the *disulphonamide*, $C_{28}H_{21}O_6NS_2$, in yellowish-brown crystals, m. p. 256° (corr.), whereas methyl sulphate yields *toluene-p-sulpho-2-anthraquinonylmethylamide* in yellow crystals, m. p. 195° (corr.), from which 2-*methylaminoanthraquinone*, $C_{14}H_7O_2 \cdot NHMe$, may be obtained in long, ruby-red needles, m. p. 226—227° (corr.), by warming with concentrated sulphuric acid. When condensed with ethylene dibromide in a sealed tube, the original sulphonamide yields *ethylenebistoluene*-p-*sulpho* - 2- *anthraquinonylamide*, $C_{44}H_{32}O_8N_2S_2$, in yellow crystals, m. p. 301° (corr.), which on hydrolysis with concentrated sulphuric acid give *ethylenebis-2-aminoanthraquinone*,

$$C_6H_4 <^{CO}_{CO}> C_6H_3 \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH \cdot C_6H_3 <^{CO}_{CO}> C_6H_4.$$
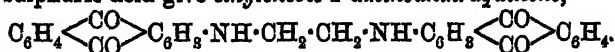
This forms small, orange-yellow crystals, m. p. 400°, and gives a red vat with sodium hyposulphite, cotton being dyed orange.

Fuming sulphuric acid (18—20% SO_3) converts 2-aminoanthraquinone into 2-*aminoanthraquinone-3-sulphonic acid*, $C_{14}H_9O_5NS$, a faintly yellow powder, which forms a white sulphate by the addition of water to the red solution in concentrated sulphuric acid, and also a golden-yellow *sodium* salt. Its constitution is determined by the formation of Scholl's 1 : 3-dibromo-2-aminoanthraquinone [A., 1907, i, 541, m. p. 249·5° (corr.), and not 239°] under the influence of bromine water, and the transformation into 2-chloroanthraquinone by eliminating the amino-group and then replacing the sulphonic group through the medium of sodium chlorate and hydrochloric acid.

The chief product of the nitration of 2-acetylaminoanthraquinone is 1-*nitro-2-acetylaminoanthraquinone*, $C_{16}H_{10}O_5N_2$, which forms long, silvery needles, m. p. 277—278° (corr.), and is hydrolysed by warm concentrated sulphuric acid to 1-nitro-2-aminoanthraquinone, m. p. 310° (corr.) (Terres, this vol., i, 738, gives m p. 267°). Bayer & Co. (A., 1906, i, 677) also obtained the latter compound by nitrating the carbamate of 2-aminoanthraquinone, m. p. 279—280°, and hydrolysing the carbamate of 1-nitro-2-aminoanthraquinone, m. p. 205°. The addition of glacial acetic acid to the solution in fuming nitric acid, however, precipitates the isomeric *carbamate* of 3-*nitro-2-amino-anthraquinone*, $C_{17}H_{12}O_6N_2$, in faintly yellow needles, m. p. 225° (corr.), thus affording a means of obtaining 3-nitro-2-aminoanthraquinone (Scholl, A., 1905, i, 70). When the 1-nitroamine or the urethane is reduced with sodium sulphide, 1 : 2-diaminoanthraquinone is obtained, m. p. 303—304° (compare Terres, *loc. cit.*). Reduction of the acetylated base, however, gives rise to 2-*methyl-a-anthraquinoneiminazole* (annexed formula). This crystallises in yellow leaflets, m. p. 326° (corr.), which form a colourless hydrochloride and an orange-red sodium salt.
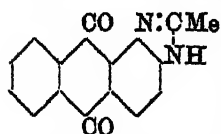
1 : 3-Dibromo-2-aminoanthraquinone condenses with *p*-toluidine in presence of anhydrous potassium acetate to form 3-*bromo-2-amino-1-toluidinoanthraquinone*, $C_{21}H_{15}O_2N_2Br$, in long, dark red, sparkling needles, m. p. 181° (corr.), which on oxidation with lead peroxide yields

3-bromoanthraquinone-1 : 2 : 1′ : 2′ : 4′-*methylphenazine*,

$$C_6H_4 <^{CO}_{CO}> C_6HBr <^N_N> C_6H_3Me,$$
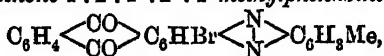
in pale brown needles, m. p. 247° (corr.). The dye gives a blue hyposulphite vat which colours cotton light blue, but the shade changes to pale yellow in the air. **J. C. W.**

Preparation of Nitroaminoanthraquinones. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 259432).—When the anthraquinone-nitroamines (A, 1905, i, 447) are treated with mineral acids (such as hydrochloric or phosphoric) they are converted into nitroaminoanthraquinones; thus anthraquinone-1-nitroamine (*loc. cit.*) when left in contact with concentrated sulphuric acid for one hour furnishes a mixture of 1 : 2- and 1 : 4-nitroaminoanthraquinones.

Anthraquinone-2-nitroamine prepared by the action of sodium hypochlorite on anthraquinone-2-*iso*diazoxide yields 1-nitro-2-amino-anthraquinone (A., 1906, i, 677), and this on reduction (by ordinary methods) gives rise to 1 : 2-*diaminoanthraquinone*, m. p. 242—244°.

Anthraquinone-1 : 5-dinitroamine furnishes a mixture of 2 : 6-dinitro- and 4 : 8-dinitro-1 : 5-diaminoanthraquinones, whilst anthraquinone-2 : 6-dinitroamine gives rise to 1 : 5-*dinitro*-2 : 6-*diaminoanthraquinone*, brown crystals, m. p. over 300°, which on reduction yields 1 : 2 : 5 : 6-*tetra-aminoanthraquinone*. **F. M. G. M.**

1 : 2-Diaminoanthraquinone and a Synthesis from it of Indanthrene. ERNST TERRES (*Ber.*, 1913, **46**, 1634—1647).—Indanthrene can be obtained from 1 : 2-diaminoanthraquinone and 1 : 2-anthraquinone, and the author also describes other angular azines obtained by the interaction of 1 : 2-diaminoanthraquinone with diethyl oxalate, benzil, 1 : 2-naphthaquinone, and phenanthraquinone. The two last-named have already been obtained (Farbenfabriken vorm. Friedr. Bayer & Co., A., 1906, i, 905). The nomenclature employed is that proposed in a former paper (Bally and Scholl, *Ber.*, 1911, **44**, 1662). The paper also records a reducing action of potassium copper cyanide, which reacts with 2-methylanthraquinonyl-1-diazonium sulphate, yielding 2-methylanthraquinone. The nitrile simultaneously formed is removed by saponifying it to the corresponding acid, which is soluble in water.

In order to exclude the formation of isomeric products, 1 : 2-diamino-anthraquinone was made (but with poor yield) by a new method, starting from 1-nitro-2-methylanthraquinone. Oxidation of this substance (best effected by concentrated nitric acid and chromic anhydride. Badische Anilin- & Soda-Fabrik, D.R.-P. 228394) yields 1-nitroanthraquinone-2-carboxylic acid, m. p. 283°. On treatment of this acid with sodium sulphide solution on the water-bath, 1-*amino-anthraquinone*-2-*carboxylic acid*, $C_{15}H_9O_4N$, is obtained; it forms brownish-red, shimmering needles, m. p. 286°. When 1-nitroanthra-quinone-2-carboxylic acid is boiled for several hours with phosphorus pentachloride in benzene solution, the acid *chloride* (which crystallises in yellow needles) is produced, and if the reaction mixture is poured into cold alcoholic ammonia solution, the *amide*, $C_{15}H_8O_5N_2$, is

obtained ; it forms yellow leaflets or large, almost colourless prisms, m. p. 299—301°.   On reduction with ammonium sulphide, the amide yields 1-*aminoanthraquinone*-2-*carboxylamide*, $C_{15}H_{10}O_3N_2$, which crystallises in red needles, m. p. 279—281°.   2-Amino-1-nitroanthraquinone, m. p. 266—267° (Farbenfabriken vorm. Friedr. Bayer & Co., A., 1906, i, 677) can be obtained from 1-nitroanthraquinone-2-carboxylic acid by warming it with bromine, potassium hydroxide, and water, but it is necessary that the acid should be freshly precipitated (by pouring an acetic acid solution of it into water).   1 : 2-Diaminoanthraquinone is obtained by heating 2-amino 1-nitroanthraquinone with ammonium sulphide solution for five hours on the water-bath.

When a mixture of 1 : 2-diaminoanthraquinone and 1 : 2-anthraquinone in acetic acid is boiled, transbisangular *anthroanthraquinone-azine* (annexed formula) is rapidly deposited as a brownish-red, crystalline paste.   It gives a dark green solution in cold, concentrated sulphuric acid, and from this solution water precipitates at first the dark blue sulphate.   In concentrated nitric acid the substance dissolves, giving a bluish-green solution, which becomes blue and finally wine-red on warming.   Alkali hyposulphite solution yields an insoluble, bluish-green vat salt.   It is possible that the above product contains also the *cis*-isomeride.   That the *trans*-form is present is shown by the fact that, by oxidation with chromic acid to anthraquinoneazine and reduction of the latter by means of boiling quinoline, indanthrene is obtainable, although only in very minute quantities and by working in very definite conditions.
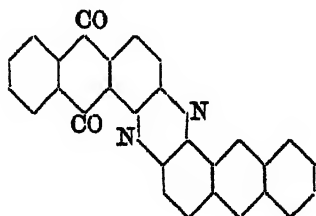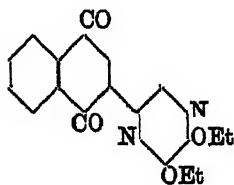
Condensation of ethyl oxalate with 1 : 2-diaminoanthraquinone (by boiling in acetic acid solution) yields 2 : 3-*diethoxypyrazinoanthraquinone* (annexed formula), which crystallises in red needles, m. p. 276—277°.   This azine gives a bright yellow solution in sulphuric acid. With hyposulphite solution it yields a red vat, which has, however, little affinity for unmordanted vegetable fibres.
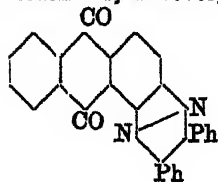
Benzil yields by a similar condensation 2 : 3-*diphenylpyrazinoanthraquinone* (annexed formula), which forms yellow needles, m. p. 282—283°.   Concentrated sulphuric acid dissolves the substance with production of a dark reddish-brown coloration.   Alkali hyposulphite yields a bluish-black, insoluble vat salt.   R. V. S.

Preparation of Anthraquinone Derivatives Containing Halogens.   FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D R.-P. 258556).—When 1 : 4-diamino- or 1-amino-4-hydroxy-anthraquinone is treated with chloric acid it furnishes a chlorinated quinone.

1 : 4-Diaminoanthraquinone (50 parts) dissolved in concentrated sulphuric acid (1000 parts) at 5° is slowly treated during about four hours with finely powdered potassium chlorate (250 parts); the *product*, a grey powder, crystallises from xylene, contains 23·1% of chlorine, and no nitrogen.

By modifying the reaction, a *compound* (I) having a higher chlorine content is obtained, and when diaminoanthrarufin (46 parts) with potassium chlorate (450 parts) is employed it gives rise to *tetrachlorotriquinone* (II) :

(I.) and (II.)
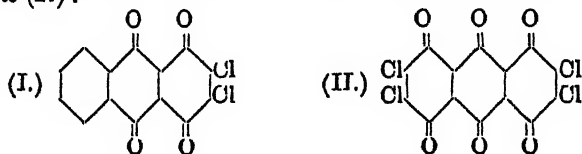
These compounds condense with aromatic amines (eliminating one atom of chlorine), furnishing dyes.   F. M. G. M.

[Derivatives of] Some Aromatic Diketones. LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 517—519).—When phenanthraquinone is boiled with an ethereal solution of diazomethane until no more diazomethane remains, nitrogen is evolved, and a *substance*, $C_{15}H_{10}O_2$, is formed ; it crystallises in thin, orange-yellow needles, m. p. 167°. The compound is stable towards permanganate.   R. V. S.

The Aliphatic Sequiterpene-Alcohol, Farnesol. MAX KERSCHBAUM (*Ber.*, 1913, **46**, 1732—1737).—The author has investigated a number of derivatives of farnesol, an alcohol which is widely distributed in flower-blossom oils (compare A., 1904, i, 513 ; Soden and Treff, A., 1904, i, 439).

Farnesol, obtained from *Hibiscus Abelmoschus*, L., and purified by the phthalic ester method, has b. p. 160°/10 mm., D^{18} 0·885, n_D 1·48809, $a_D \pm 0°$. It may be preserved in closed vessels for years without alteration. Solid derivatives have not been obtained. The *acetate* has b. p 169—170°/10 mm., and is practically odourless. When heated with potassium hydrogen sulphate at 160—170°, farnesol loses water, form'ng *farnesene*, a colourless, mobile oil, b. p. 129—132°/12 mm., D^{18} 0·877, n_D 1·49951, $a_D \pm 0°$. Oxidation of farnesol by means of chromic acid and dilute sulphuric acid leads to the formation of farnesaldehyde, which, after purification by means of the solid bisulphite *compound*, has b. p. 172—174°/14 mm., D^{18} 0·893, n_D 1·49951, $a_D \pm 0°$. The corresponding *semicarbazone*, leaflets, m. p. 133—135° after slight previous softening, is well adapted for the identification of farnesol.

Attempts to determine the constitution of farnesol by a study of the products of the action of potassium permanganate on it were not completely successful. Acetone was, however, isolated. When, however, *farnesaldoxime* was converted into the corresponding *nitrile* and the latter saponified by alcoholic sodium hydroxide, *farnesenic acid*, b. p. 202—206°/16 mm., acetic acid, and a ketone were obtained. The latter substance was identified as dihydro-ψ-ionone by

means of its semicarbazone. Since the constitution of the latter follows from its synthesis from geranyl chloride and ethyl sodio-acetoacetate followed by saponification of the ethyl geranylaceto-acetate by sodium hydroxide, the following formula is ascribed to farnesol : $CMe_2:CH\cdot[CH_2]_2\cdot CMe:CH\cdot[CH_2]_2\cdot CMe:CH\cdot CH_2\cdot OH$ (compare following abstract).

Dihydro-ψ-ionone is converted by methyl magnesium bromoacetate into a *methyl hydroxydihydrofarnesenate*, which, on prolonged heating with acetic anhydride and sodium acetate at 160—165°, loses water, and yields *methyl farnesenate*, b. p. 177—185°/10 mm. The corresponding free acid has a b. p. identical with that of the acid obtained from farnesol. Solid derivatives could not, however, be prepared.

Reduction of methyl farnesenate by sodium and absolute alcohol gives rise to a mixture of dihydro-ψ-ionol. dihydrofarnesol, and, probably, farnesol. The presence of the latter could not, however, be definitely established.   H. W.

Farnesol. CARL HARRIES and REINHOLD HAARMANN (*Ber.*, 1913, **46**, 1737—1741).—A study of the action of ozone on farnesol has confirmed the formula ascribed to the latter by Kerschbaum (preceding abstract).

When farnesol is ozonised in hexane solution, a gelatinous *diozonide* is obtained, which, on further treatment with azone in chloroform solution, is transformed into the *triozonide*. The latter, when boiled with water, gave the tests for hydrogen peroxide, for the group $C\cdot CO\cdot C\cdot C\cdot CHO$ and for aldehydes, whilst acetone, formic and acetic acids, lævulinaldehyde, and lævulic acid were identified among the products formed.

The action of ozone on farnesene was also investigated, the latter substance having been obtained by the fractionation of a specimen of crude farnesol which had been preserved during several years and which had undergone decomposition to a considerable extent with elimination of water. In carbon tetrachloride solution, the hydrocarbon yields a stable, glassy *tetra-ozonide*, which is decomposed by boiling water with formation of lævulinaldehyde. The latter was identified by conversion into phenylmethyldihydropyridazine, m. p. 197° (Harries, A., 1898, i, 233).   H. W.

Methylcamphoroxime,   Methylcampholenonitrile,   and Methylcampholenic Acid. ALBIN HALLER and ÉDOUARD BAUER (*Compt. rend.*, 1913, **156**, 1503—1506).—The mixture of methyl- and dimethyl-camphor obtained by the action of methyl iodide on sodium camphor (compare A., 1909, i, 594) can be separated by the action of hydroxylamine zinc chloride, the methylcamphor being converted into its oxime, m. p. 60°, b. p. 134—135°/11 mm., $[\alpha]_D^{22} +25\cdot15°$ (compare Glover, T., 1908, **93**, 1285). It gives a *phenylurethane*, prismatic crystals, m. p. 112—113°, $[\alpha]_D^{22} +24\cdot8°$, and at the same time a small quantity of slender needles, m. p. 110—111°, which are inactive. The oxime is hydrolysed by hydrochloric acid into the nitrile, b. p. 105—106°/15 mm., $[\alpha]_D^{22} +45°$ (compare Glover, *loc. cit.*). In solution in alcohol it has $[\alpha]_D^{23} +53\cdot9°$. The nitrile is hydrolysed by

alcoholic potassium hydroxide to *methylcampholenamide*, m. p. 91—92°, which is completely inactive, and this in its turn is hydrolysed by more concentrated alkali to *methylcampholenic acid*, m. p. 30°, b. p. 153°/ 20 mm., which is also inactive. It is probable that the methylcampholenonitrile by reason of its optical activity is analogous to a-campholenonitrile, but in the course of hydrolysis undergoes transformation, its derivatives being of the β-type. W. G.

*iso*Nitroamines of the Terpenes. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 616—622. Compare Cusmano and Linari, A., 1912, i, 272) —*Carvomenthone-aβ-hydroxylamineoxime* (annexed formula) is obtained by the action of hydroxylamine on carvomenthone bisnitroso-chloride ; it forms tufts of long, colourless needles, m. p. 118°. From the mother liquor the following substances can be isolated in small quantity : active carvotanacetoneoxime, oxytetrahydrocarvoneoxime, and two other *oximes* of m. p. 120° and 160° respectively. The hydroxylamineoxime reduces ammoniacal silver nitrate and Fehling solution. When treated with ferric salts, it yields an amorphous, yellow powder, which is soluble in ether and contains iron. This *substance* gives Liebermann's reaction, and when shaken in ethereal solution with concentrated hydrochloric acid, it loses its iron, and is converted into a blue *compound*. The hydroxylamineoxime yields a *benzylidene* derivative, $C_{17}H_{23}O_2N_2$, which crystallises in hard, colourless prisms, m. p. 141°. The p-*nitrobenzylidene* derivative is a yellow powder.
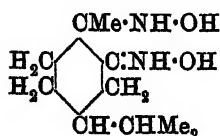
CMe·NH·OH
H_2C C:NH·OH
H_2C CH₂
CH·CHMe₂

Carvomenthone-aβ-isonitroamineoxime, $C_{10}H_{19}O_3N_3·H_2O$, obtained by the action of sodium nitrite on the hydrochloride of the hydroxylamineoxime above described, forms rectangular tablets, m. p. 64°. It gives blue colorations with sulphuric acid solutions of phenol and diphenylamine. The *ammonium* and *silver* salts were prepared. When the aqueous solution of the *potassium* salt is boiled, the active oxime of carvotanacetone is produced. The *iso*nitroamineoxime is fairly stable towards acids ; after prolonged boiling with acetic acid or hydrochloric acid only small quantities of tanacetone are formed. When the *iso*nitroamineoxime is dissolved in the equimolecular quantity of potassium carbonate and the solution is placed over sulphuric acid, nitrous oxide is evolved, and the *salt* of oxycarvomenthoneoxime is produced. If this is decomposed with carbonic acid, the *oxime*, $C_{10}H_{18}O(NOH)$, is obtained in rhomboidal leaflets, m. p. 102°. On evaporating a solution of the oxime in ethyl nitrite the *pernitrosyl* compound is deposited as an oil, and this reacts with semicarbazide to form *oxycarvomenthonesemicarbazone*, m. p. 172°.

If concentrated methyl-alcoholic solutions of hydroxylamine and 8-*iso*nitroaminomenthone are mixed (being cooled meanwhile with ice and salt) the *hydroxylammonium* salt, $C_{10}H_{18}O_3N_2·NH_2·OH$, is precipitated in long, colourless needles, m. p. 68°. Acids decompose the salt in the cold, yielding the original *iso*nitroamine, whilst cold alkalis convert it into pulegone. The salt remains unaltered for a long time in the solid state, but in alcoholic or ethereal solution it is rapidly

transformed into *menthoneisonitroamineoxime*, $C_{10}H_{19}O_3N_3$, which forms large, prismatic crystals, m. p. 77°. This substance gives blue colorations with sulphuric acid solutions of diphenylamine and phenol. It is very stable towards heat, remaining unaltered for a long period at 150°. The *potassium* salt, $C_{10}H_{18}O_3N_3K,2H_2O$, explodes above 350°. The *sodium* salt, $C_{10}H_{18}O_3N_3Na,4H_2O$, has m. p. 66°, or when anhydrous, 220° (decomp.). The *ammonium* salt dissociates at about 100° into its components.   R. V. S.

The Constituents of Ethereal Oils. Synthesis of the Diterpene, α-Camphorene, $C_{20}H_{32}$, and of the Sesquiterpene *cyclo*Isoprenemyrcene, $C_{15}H_{24}$. FRIEDRICH W. SEMMLER and K. G. JONAS (*Ber.*, 1913, 46, 1566—1571. Compare Semmler and Rosenberg, this vol., i, 377).—Unsuccessful attempts have been made to synthesise α-camphorene from isoprene, and also by the addition of two isoprene radicles to limonene.

Myrcene was heated in a sealed tube at 250—260° for four hours, and the product subjected to fractional distillation, whereby a portion, b. p. 175—195°/8 mm., was obtained, analyses of which gave results agreeing with the formula $C_{20}H_{32}$. When a cooled, absolute ethereal solution of the product was saturated with dry hydrogen chloride, a crystalline product was obtained identical in all respects with α-camphorene tetrahydrochloride. Successive treatment with glacial acetic acid and sodium acetate, and with alcoholic potassium hydroxide, converted it into *o*-camphorene identical with the substance obtained from camphor oil of high boiling point, from which the tetrahydrochloride could be regenerated. The mother liquor obtained from the α-camphorene tetrahydrochloride, on treatment with glacial acetic acid and sodium acetate and, subsequently, with alcoholic potassium hydroxide, yielded other diterpenes which appeared to be bicyclic.

Since myrcene is a butadiene and undergoes condensation when heated, attempts were made to obtain a condensation product from myrcene and isoprene. When these substances were heated in a sealed tube for three and a-half hours at 225° and the product fractionated, the following fractions were obtained: (i) unchanged isoprene; (ii) b. p. 52—65°/8 mm., consisting of dipentene obtained partly from the condensation of two isoprene molecules, and partly by the isomerisation of myrcene; (iii) b. p. 120—150°/8 mm., which, on subsequent distillation, yielded cyclo*isoprenemyrcene*, b. p. 125—135°/8 mm., n_D 1·49166, $a_D \pm 0°$, D^{18} 0·8685. The latter yielded a *trihydrochloride*, m. p. 83°, from which the hydrocarbon could be regenerated in the usual manner, and again converted into the hydrochloride; (iv) b. p. 175—195°/8 mm., n_D 1·5034, $a_D \pm 0°$, D^{20} 0·8890, and (v) a considerable residue.   H. W.

The Constituents of Essential Oils. The Constitution of Zingiberene. Transformation of the Monocyclic Zingiberene into the Bicyclic *iso*Zingiberene. FRIEDRICH W. SEMMLER and A. BECKER (*Ber.*, 1913, 46, 1814—1822).—Of the naturally-occurring monocyclic sesquiterpenes, only limene and zingiberene have been studied. The former can be regenerated from its trihydrochloride, but

the latter gives a dihydrochloride which no longer yields the original oil with alkalis. The conclusion is therefore drawn that the hydrochloride contains a different ring system. In addition, the abnormal molecular refraction, 68·37 instead of 67·86, suggests that two of the three unsaturated linkings are adjacent in a side-chain.

Consequently, like myrcene, which has a similar structure and may be reduced to dihydromyrcene and readily transformed into cyclic terpenes, zingiberene (I) may be reduced to dihydrozingiberene and also converted into a dicyclic hydrocarbon. The latter is found to yield the above hydrochloride, from which it may be regenerated. It receives the name, *iso*zingiberene (II).
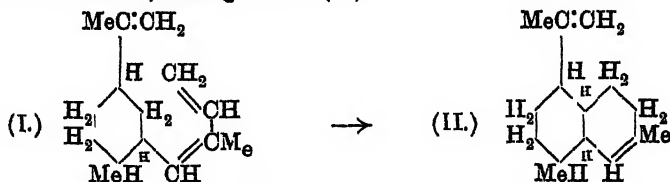
Finally, like other butadienes, zingiberene may be polymerised or condensed with isoprene.

The reduction of zingiberene (b. p. 128—129°/9 mm., D^{20} 0·8684, n_D 1·4956) by means of sodium and alcohol results in the formation of monocyclic *dihydrozingiberene*, $C_{15}H_{26}$, with b. p. 122—125°/7 mm., D^{20} 0·8557, n_D 1·4837, $[\alpha]_D$ - 37°. The complete reduction with platinum and hydrogen yields monocyclic *hexahydrozingiberene*, $C_{15}H_{30}$, with b. p. 128—130°/11 mm., D^{20} 0·8264, n_D 1·4560, $[\alpha]_D$ - 10°12'. The linking-up of the side-chain into a ring is effected by dissolving the zingiberene in glacial acetic acid containing a small amount of sulphuric acid, and agitating for some hours at 60—65°. iso*Zingiberene*, $C_{15}H_{24}$, yields the same chloride as zingiberene itself (Schreiner and Kremers, A., 1902, i, 108) and also a *dihydrobromide*, m. p. 175°, from which alcoholic potassium hydroxide regenerates the pure hydrocarbon, with b. p. 120—123°/8 mm., D^{20} 0·9150, n_D 1·5034, $[\alpha]_D$ - 41°. Reduction with platinum and hydrogen converts the substance into *tetrahydro*iso*zingiberene*, $C_{15}H_{28}$, which is similar to other bicyclic tetrahydrosesquiterpenes, and has b. p. 123—123·5°/10 mm., D^{20} 0·8822, n_D 1·4791, and $[\alpha]_D$ + 4°36'.

When heated with isoprene in a sealed tube, zingiberene gave a mixture which was fractionated, and found to contain *i*-limonene, a bicyclic, dextrorotatory, modified zingiberene, "meta-zingiberene," a diterpene from the condensation of isoprene with zingiberene, and dizingiberene.   J. C. W.

[Essential Oils.] SCHIMMEL & Co. (*Semi-Annual Report*, April, 1913, pp. 20—153. Compare A., 1912, i, 880).—First runnings from the distillation waters of angelica contained methyl alcohol, ethyl alcohol, furfuraldehyde, diacetyl, and a base having an odour of pyridine.

Angostura bark (*Cusparia trifoliata*, Engl.) yielded 1·03% of oil, D^{15}_5 0·9285, α_D^{20} - 7°32', n_D^{20} 1·50744, of pale brown colour and having

acid number 1·8, ester number 5·5, acetyl ester number 35·7 ; the oil is not completely soluble even in 9 vols. of 90% alcohol.

Arnica root oil, D_{15}^{15} 0·984—1·00, $a_D^{20} + 0°25'$—2°, n_D^{20} 1·507—1·508, had acid number 4 to 10, ester number 60 to 100, and gives a turbid solution with 7 to 12 vols. of 80% or 0·5 to 6·0 vols. of 90% alcohol. Arnica flower oil, D_{30}^{30} 0·8905 to 0·9029, acid number 62·6 to 127·3, ester number 22·7 to 32·2, is a buttery mass, m. p. 20—30° (approx.), and very sparingly soluble in alcohol.

Artemisia vulgaris, L., oil from India, had D_{15}^{15} 0·9219, $a_D^{20} - 8°52'$, n_D^{20} 1·46201, acid number 1·2, ester number 22·1, acetyl ester number 55·5, and was soluble in 1 vol. of 80% alcohol, becoming turbid and depositing crystals of a solid paraffin on further dilution. The oil was of greenish-yellow colour and sage-like odour. It contains a-thujone, and possibly borneol.

Banana fruit oil according to Kleber (*Amer. Perf.*, 1912, **7**, 235) contains amyl acetate and traces of a phenol.

Borneo camphor oil, D_{15}^{15} 0·9180, $a_D^{20} + 11°5'$, n_D^{20} 1·48847, was of dark brown colour, soluble in 5 vols. or more of 90% alcohol, and had acid number 5·6, ester number 0, acetyl ester number 50·5. It contained d-a-pinene, β-pinene, dipentene, and camphene (35% of terpenes in all), borneol, and a-terpineol (10% together), sesquiterpenes 20%, and resin 35%.

The "Camphor leaf oil" (*Cinnamomum camphora*) described previously (A., 1905, i, 537) is now stated to be from the leaves of *Cinnamomum glanduliferum*, Meissn. It contains no camphor (compare Pickles, T., 1912, **101**, 1433). An oil from a hybrid between these two species deposited 58% camphor on freezing, and then had D_{15}^{15} 1·0465, $a_D^{20} + 34°24'$, acid number 1·0, ester number 23·3, acetyl ester number 46·2, and was soluble in 0·8 vol. of 80% alcohol. It still contained camphor, but no safrole could be detected.

Further investigation of Seychelles cinnamon bark oil (A., 1909, i, 112) shows that it contains the same constituents as Ceylon cinnamon bark oil.

The comparison of various methods for the estimation of geraniol and citronellal in citronella oils has been continued (A., 1912, i, 880). Kleber's phenylhydrazine process gives the following percentage values: *Java oil*, citronellal 35—41·3, geraniol 26·6—40·1 ; *Ceylon oil*, citronellal 7·5—11·6, and geraniol 29·6—34·4. Dupont and Labaune's method gives citronellal 35·4—46·3% and 6·5—8·0% for Java and Ceylon oils respectively. Kleber's phenylhydrazine process may also be used for cuminaldehyde, benzaldehyde, and methyl nonyl ketone ; in the case of oil of bitter almonds only the free benzaldehyde reacts with phenylhydrazine. The process is being tried for the estimation of ketones in rue oil.

The two alcohols already noticed in cypress oil (A., 1904, i, 604) have been further examined : the chief constituent of the mixture is now shown to be 4-terpineol ; the second alcohol, $C_{10}H_{18}O$, has D_{15}^{15} 0·9422, $a_D^{20} + 43°38'$, n_D^{20} 1·46678, b. p. 76—77°/4—5 mm., and has a rose odour with a suggestion of borneol. The highest fractions of the oil contain in addition to cypress camphor and cadinene, a liquid

sesquiterpene *alcohol*, $C_{15}H_{26}O$, b. p. 136—138°/4—5 mm., which on treatment with formic acid yields a hydrocarbon.

Dipterocarpus turbinatus, Gaertn., oleo-resin yielded 46% of a pale yellow balsamic oil, D_{15}^{15} 0·9271, a_D^{20} − 37°, n_D^{20} 1·50070, acid number 0, ester number 1·9, soluble in 7 vols. of 95% alcohol. *D. tuberculatus*, Roxb., oleo-resin gave 33% of a yellowish-brown oil, D_{15}^{15} 0·9001, a_D − 99°40′, n_D^{20} 1·50070, soluble in 6 vols. of 95% alcohol. Both these oleo-resins and oils gave Turner's colour reaction.

Caryophyllene was detected in a French lavender oil.

Lemon-grass oils from Assam, Burma, Formosa, Celebes, and Mayotte are described : these are mostly of the "insoluble" type.

Mentha aquatica, L., herb yielded 0·8% of oil, D_{15}^{15} 0·9553, a_D^{20} + 64°56′, n_D^{20} 1·48276, of pale yellow colour and having a faint odour of mint. *Mentha sylvestris*, L., herb gave 0·9% of similar oil, D_{15}^{15} 0·9852, a_D^{20} − 132°52′, n_D^{20} 1·46856. *M. viridis* herb gave 0·17% of oil, D_{15}^{15} 0·9512, a_D^{20} − 52°5′.

Mosla Japonica, Max., oil according to Nurayama and Nara (*J. pharm. Soc. Japan*, 1912) contains a-pinene (compare A., 1910, i, 328).

Ocotea pretiosa, Benth., bark gave 0·83% of a brown oil, D_{15}^{15} 1·1200, n_D^{20} 1·52712, soluble in 6·5 vols. of 88% alcohol, and having a cinnamon-like odour. The oil is nitrogenous, contains no cinnamaldehyde, but probably contains caryophyllene, phenols, and lactones.

d-Ethyl-*n*-amylcarbinol from Japanese peppermint oil (A., 1912, i, 370) yields a *benzoate*, D_{15}^{15} 0·9641, a_D^{20} + 5°58′, n_D^{20} 1·48905, b. p. 126·5°/ 3 mm., which is viscous, colourless, and possesses a faint odour. The *acetate*, D_{15}^{15} 0·8693, a_D^{20} − 4°46′, n_D^{20} 1·41535, b. p. 194—194·5°/760 mm., has a peculiar odour of fruit and roses. The inactive modification of the alcohol, D_{15}^{15} 0·8286, n_D^{20} 1·42785, b. p. 176—177·5°, has been synthesised by the action of magnesium ethyl iodide on *n*-hex-aldehyde.

Rhus Cotinus, L., leaves and flowers yielded a very pale yellow oil, D_{15}^{15} 0·8710, a_D^{20} + 32°54′, n_D^{20} 1·4887, acid number 0·9, ester number 20·4, soluble in 6 vols. 90% alcohol, and having an odour of terpenes, but slightly suggestive of neroli ; it contained camphene, β-pinene (?), and limonene ; no phellandrene or terpinene could be detected.

Amomum globosum fruits ("wild cardamoms") from Indo-China yielded 4% of a colourless oil, D_{15}^{15} 0·9455, a_D^{20} + 43°54′, n_D^{20} 1·47141, acid number 0·8, ester number 128·4, insoluble in 10 vols. of 70% alcohol, but soluble in 1 vol. of 80% alcohol and having a strong odour of camphor.

Cherry stones when ground and left for several hours furnished, on steam distillation, 0·016% of an oil, D_{15}^{15} 1·0532, a_D^{20} 0°, n_D^{20} 1·53888, soluble in 2·5 vols. of 60% alcohol, having an odour similar to, but clearly different from, that of bitter almond oil, and containing 0·27% of hydrocyanic acid.

Fennel herb from Jersey yielded an oil, D_{15}^{15} 0·9561, a_D + 16°40′, soluble in 5 vols. 80% alcohol. Its odour indicated that methyl-chavicole was the chief constituent, and that very little anethole was present.

Meum athamanticum, Jacq., herb from the Harz mountains yielded

0·88% of a deep reddish-brown oil, D_{15}^{17} 0·9053, n_D^{20} 1·50327, acid number 8·8, ester number 63·1, soluble in 3 vols. of 90% alcohol, which had a celery-like odour, and on keeping deposited crystals, m. p. 91° (guaiacol?)

The Report also contains a résumé of recent work on the chemistry, pharmacology, etc., of essential oils and their constituents.

<div style="text-align:right">T. A. H.</div>

[Essential Oils.] ROURE-BERTRAND FILS (*Sci. Ind. Bull.*, 1912, [iii], **6**, 3—191 ; 1913, [iii], **7**, 3—147).—*Calamintha Nepeta*, Lk. and Hoff., grown in Sicily, yielded 0·1426% of a brown oil, D_{17}^{17} 0·9249, a_D +17°48′, acid number 1·4, saponification number 12·6, which has an odour of pennyroyal, is soluble in 0·5 or more vols. of 80% alcohol, contains 20% of pulegone and 14% of alcohols, with a considerable quantity of a second ketone (menthone?).

Lemon grass oils from Mayotte, distilled from *Cymbopogon citratus*, had D_{15}^{17} 0·8877—0·9072, a −0°4′—0°6, aldehydes 75·5 to 78% and were insoluble in 90% alcohol.

Basil oils from Mayotte had D_{15}^{17} 0·9630—0·9677, a_D +0°56′—0°58′, acid number 0·7 to 1·4, saponification number 5·6 to 6·3, esters 1·9 to 2·2%, and were soluble in 3·0 to 3·2 or more vols. of 80% alcohol. These oils had an odour of anethole as well as of estragol.

[JUSTIN DUPONT and LOUIS LABAUNE.]—With a view to ascertaining the cause of the anomalous results obtained in estimating aldehydes in essential oils by means of sodium hydrogen sulphite solution, the authors have investigated the action of such solutions on a large number of common unsaturated constituents of essential oils and find that many of these are wholly or partly converted into hydro-sulphonates when shaken for some time with aqueous solutions of sodium hydrogen sulphite. Among the unsaturated substances which do not react in this way are hydrocarbons (for example, *l*-pinene, limonene, and styrene), esters, ethers, *iso*eugenol, and ionones. The results with all the substances examined are tabulated in the original. The following were isolated, the *sodium hydrogen sulphite* compounds of *geraniol* $C_{10}H_{18}O,2NaHSO_3$; *linalool*, $C_{10}H_{18}O,2NaHSO_3$; *terpineol*, $C_{10}H_{18}O,NaHSO_3$; *methylheptenone*, $C_8H_{14}O,NaHSO_3$; they are all hygroscopic masses (compare Labbe, A., 1900, i, 149), and are stable, since they do not regenerate the original organic constituent on addition of alkali. In a second paper on the analysis of citronella oil the authors point out that in Boulez's method for the assay of this oil (A., 1912, ii, 1105 ; Schimmel & Co., A., 1912, i, 880), the results for citronellal are liable to be rendered inaccurate by the absorption of a larger or smaller portion of the geraniol in the hydrogen sulphite solution.

Both "Bulletins" contain summaries of work recently published on essential oils.

<div style="text-align:right">T. A. H.</div>

Theory of the Vulcanisation of Caoutchouc. II. GUSTAV BERNSTEIN (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 273—277. Compare A., 1912, ii, 1007).—A continuation of the discussion of the theory of vulcanisation. It is shown that before vulcanisation occurs

a depolymerisation of the caoutchouc must take place, and that at the same time a polymerisation of the sulphur occurs. These two changes are shown to take place under the same conditions, whether the vulcanisation is effected by heat or by ultra-violet light. It is stated that the absorption of sulphur begins only when it has been converted into the insoluble form. It is also stated that the physical properties of the vulcanised product depend on the condition of aggregation of the caoutchouc at the moment of the formation and absorption of the insoluble sulphur. J. F. S.

Biochemical Synthesis of Alkylglucosides (a-Glucosides) by means of a Ferment (a-Glucosidase) contained in Air-dried, Bottom Yeast: a-Propylglucoside and a-Allylglucoside. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and MARC BRIDEL (*Compt. rend.*, 1913, **156**, 1493—1495; *J. Pharm. Chim.*, 1913, [vii], **7**, 525—529. Compare this vol., i, 323, 428).—a-*Propylglucoside*, crystallising in long needles, having a bitter taste, $[a]_D$ +140·8°, and a-*allylglucoside*, colourless needles, m. p. 85—90°, $[a]_D$ +131·72°, are obtained by the action of a-glucosidase on solutions of dextrose in water containing 15% of the respective alcohols. They are both very soluble in water, and are readily hydrolysed in aqueous solution by the above ferment.
W. G.

Biochemical Synthesis, by means of Emulsin, of a Glucoside Isomeric with Salicin, β-Salicylglucoside. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1913, **156**, 1790—1792).— Emulsin acts on a solution of salicyl alcohol and dextrose in acetone, containing 20% water, giving β-*salicylglucoside*, which is finally obtained crystallising in long, colourless needles, $[a]_D$ −37 5°, the melting point varying considerably with the rate of heating. It is odourless, but possesses a bitter taste and is soluble in water, crystallising with $4H_2O$. It reduces Fehling's solution and gives a violet colour with ferric chloride, which does not disappear on shaking with ether. The yield of glucoside varies with the dilution of the acetone and the amounts of alcohol and dextrose used, the presence of an excess of alcohol favouring the synthesis. The glucoside is readily hydrolysed in aqueous solution by emulsin. W. G.

Cerebrosides of the Brain. III. HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1913, **85**, 35—58. Compare Loening and Thierfelder A., 1911, i, 898; 1912, i, 372).—Prolonged treatment of cerebrone with barium hydroxide is shown not to produce any marked change. The cerebrone fraction is found to consist of a crystalline and an amorphous component which have the same composition and optical rotatory power, but differ in solubility. The name cerebrone is retained for the crystalline substance and that of phrenosin restricted to the amorphous form. In addition to the cerebrone fraction the use of a mixture of chloroform and methyl alcohol as solvent resolves the mixed cerebrosides into a very soluble fraction and a fraction of intermediate solubility to which the term kerasin is applied. Acid hydrolysis of

this fraction shows it to be broadly similar to cerebrone. It yields about 20% of galactose, some quantity of dimethylsphingosine as sulphate, and *kerasinic acid*, $C_{24}H_{48}O_2$, which crystallises in slender, long needles, m. p. 77—78°.   E. F. A.

New Derivatives of Artemisin and Santonin. ENRICO RIMINI and TEMISTOCLE JONA (*Chem. Zentr.*, 1913, i, 1773; *from Rend. Soc. Chim. Ital.*, 1913, 5, ii, 52—53. Compare Weinhaus and Oettingen, this vol., i, 474, and Wedekind and Beniers, this vol., i, 476).—These substances have been reduced by Paal's method. *Tetrahydroartemisin*, $C_{15}H_{22}O_4$, forms lustrous leaflets, m. p. 192—193°, and tetrahydrosantonin has m. p. 153—155°. Both compounds are stable towards permanganate.   J. C. W.

"Tecomin." OTTO A. OESTERLE (*Arch. Pharm.*, 1913, 251, 301—303).—The colouring matter described under this name by Lee (T., 1901, 79, 284) as occurring in the wood of *Bignonia tecoma* (Ipé wood or Ipé-tabaco wood) is now shown to be lapachol. The latter also occurs in the timbers of *Tecoma Ipé*, Mart. (Ipé preto), and *Tecoma ochracea* (Ipé amarillo), but not in greenheart wood, derived from *Nectandra Rodiaei.* The usual source of lapachol is "Surinam greenheart" derived from *Bignonia leucoxylon* (compare Stein, *Jahresb.*, 1866, 651).   T. A. H.

[**Bibirubic Acid and Derived Substances.**] HANS FISCHER (*Ber.*, 1913, 46, 1574—1577. Compare Piloty, this vol., i, 500).—Polemical. In regard to disputed questions of nomenclature, the author's proposals are as follow : (1) the acid $C_{17}H_{24}O_3N_2$ (Fischer and Röse, A., 1912, i, 575) is bilirubic acid ; (2) the acid $C_9H_{13}O_2N$ (Piloty and Thannhauser, A., 1912, i, 736) is *iso*phonopyrrolecarboxylic acid ; (3) if, as is probable, xanthobilirubic acid is identical with Piloty's dehydrobilirubic acid (dehydrobilic acid, Piloty and Thannhauser, A., 1912, i, 925), then the latter name should be adopted.   R. V. S.

Constitution of Lutein. CESARE SERONO (*Chem. Zentr.*, 1913, i, 1198; *from Arch. Farmacol. Sperim.*, 1912, 14, 509—511. Compare A., 1911, ii, 1005).—The opinion expressed by Willstätter and Escher that lutein from the yolks of eggs is a xanthophyll (A., 1912, i, 125) cannot be reconciled with that of the author who believes it to be an ethereal combination of cholesterol with unsaturated fatty acids.
       J. C. W.

Angostura Alkaloids. Decomposition Experiments with Cusparine. JULIUS TROGER and W. BECK (*Arch. Pharm.*, 1913, 251, 246—290. Compare A., 1912, i, 895).—Further analyses of cusparine and of its derivatives show that this alkaloid has the formula $C_{19}H_{17}O_3N$ (compare Körner and Böhringer, A., 1884, 341, and Troger and Muller, A., 1910, i, 414). Further descriptions of the purification of this alkaloid and of the isolation of galipoidine and of a new alkaloid are given.

Cusparine, $C_{19}H_{17}O_3N$, appears to be trimorphic, since in addition

to the two forms already described (*loc. cit.*, and A., 1911, i, 482) a third crystallising in long, pale yellow needles, m. p. 91—92°, was obtained by slow crystallisation from light petroleum. The oxalate, $B,C_2H_2O_4,1\frac{1}{2}H_2O$, m. p. 140—150°, crystallises in sulphur-yellow needles from water and is efflorescent. The *succinate*, $B_2,C_4H_6O_4,4\frac{1}{2}H_2O$, m. p. 80°, crystallises in greenish-yellow needles, loses water on standing in a desiccator and becomes anhydrous and colourless when crystallised from alcohol and then melts at 113°. The *malate*, $B,C_4H_6O_5$, m. p. 152°, forms heavy, prismatic crystals from water. The *tartrate*, $B,C_4H_6O_6,1H_2O$, m. p. 161—162°, forms yellow, microscopic crystals from water. The *citrate*, $B,C_6H_8O_7$, m. p. 174° (decomp.), crystallises in long, sulphur-yellow, prismatic needles. All these organic salts on melting yield pyrocusparine, $C_{18}H_{15}O_3N$, m. p. 255°, which crystallises from alcohol in masses of slender, colourless needles (compare Beckurts and Frerichs, A., 1904, i, 84), and yields well-crystallised salts: *hydrochloride*, B,HCl, m. p. 207°, stellate groups of colourless needles; *platinichloride*, B_2,H_2PtCl_6, m. p. above 150° (decomp.), reddish-yellow, glancing needles. Cusparine methiodide, m. p. 190°, yellow prisms; *ethiodide*, m. p. 206—212°, yellowish-brown, prismatic crystals, and the n-*propyl iodide*, m. p. 187° (decomp.), yellow prisms, were prepared. These on treatment with silver hydroxide or potassium hydroxide do not yield as Beckurts supposed (A., 1896, i, 66) the corresponding alkylcusparines, but the same *isomeride* of cusparine, m. p. 194°, crystallising from alcohol in colourless, prismatic needles, containing water of crystallisation, which is lost at 105°. This substance yields a *platinichloride*, m. p. 185° (approx.), crystallising in microscopic needles and with nitric acid yields a *nitro*-compound, $C_{19}H_{16}O_5N_2$, m. p. 234—235°, which forms greenish-yellow crystals from alcohol. Cusparine is optically inactive, does not react with hydroxylamine, yields no definite products when treated with acids or alkalis in closed vessels at 100° and in common with pyrocusparine and "nitrocusparine" (Tröger and Runne, A., 1911, i, 482) contains no ·OH group. When heated for several days at 100° with nitric acid (D = 1·075), cusparine yields an *acid*, $C_{10}H_7O_3N,H_2O$, m. p. 271—272°, which is probably a hydroxyquinolinecarboxylic acid, since on heating at 300° it loses carbon dioxide and furnishes a *base* from which a *platinichloride*, $(C_9H_7ON)_2,H_2PtCl_6,2H_2O$, m. p. 220° (decomp.), forming yellowish-red crystals, was obtained. On distillation over zinc dust the acid yielded quinoline (identified by means of the platinichloride). On the basis of these results a skeleton-formula for cusparine is suggested.

When galipoidine is examined by Zeisel's method it yields less methyl iodide than is required for ·OCH₃ in the formula $C_{19}H_{15}O_4N$ (A., 1911, i, 482).

In the purification of cusparine a fourth *alkaloid*, $C_{10}H_{13}O_2N$ (?), m. p. 186°, crystallising from boiling alcohol in sulphur-yellow, rhombic crystals was obtained.　　　　　　　　　　　　　　　　　　　　　　　T. A. H.

Carpiline or Pilosine. ÉMILE LÉGER and FERDINAND ROQUES (*Compt. rend.*, 1913, 156, 1687—1689).—The two bases, one soluble and the other insoluble in water, obtained by heating carpiline with

water in a sealed tube at 140° for ten hours (compare this vol., i, 83), are shown to be identical with the pilosinine and anhydropilosine of Pyman (compare T., 1912, **101**, 2260).   W. G.

Ephedrine. ERNST SCHMIDT (*Arch. Pharm.*, 1913, **251**, 320).—It is shown that the asymmetry of ephedrine and ψ-ephedrine cannot be solely dependent on the ·CH(OH)· group, since the conversion of this into a ·CH$_2$· group does not destroy the optical activity.

A *base*, C$_{10}$H$_{15}$N (hydrochloride has $[a]_D$ +19·14°), has been prepared by treating ephedrine hydrochloride with phosphorus pentabromide and reducing the *bromide*, C$_{10}$H$_{14}$NBr,HBr (glistening leaflets), with zinc and hydrochloric acid. This bromide on treatment with silver nitrate does not regenerate ephedrine, but gives ψ-ephedrine, m. p. 117°, $[a]_D$ +49·45° (compare A., 1912, i, 644). The optical activity of the base C$_{10}$H$_{15}$N must be due to the ·CHNMe group (compare Emde, A., 1909, i, 77; Gadamer, *ibid.*, i, 49), which, moreover, cannot be situated at the end of the ·C$_3$H$_7$ chain.   T. A. H.

The Homologues of Morphine, Codeine and Dionine, and Some of their Derivatives. FRIEDRICH FERREIN (*Chem. Zentr.*, 1913, i, 1696—1698).—Attempts have been made to prepare a hydroxycodeine by the elimination of the amino-group from amino-codeine and to obtain nitroethyl- and aminoethyl-morphine. Vonger-ichten and Weilinger (A., 1905, i, 542) obtained diacetylaminocodeine by the reduction of nitrocodeine with tin and acetic acid, whereas the *mono*-derivative, C$_{20}$H$_{24}$O$_4$N$_2$, has now been obtained by the same method. It yields a hydrochloride and a sulphate, and also *acetylamino-codeine methiodide*, C$_{21}$H$_{27}$O$_4$N$_2$I, as a white substance, m. p. 215—216°, which is converted into triacetylaminomethylmorphol (*ibid.*) on heating with acetic anhydride and silver acetate. When nitrocodeine is reduced by stannous chloride, however, the product is *aminocodeine*, C$_{18}$H$_{22}$O$_3$N$_2$, which forms pale yellow crystals, m. p. 224°, and gives what is probably a hydroxy-compound on diazotising and warming.

Ethylmorphine (dionine) has also been nitrated. *Nitroethylmorphine*, C$_{19}$H$_{22}$O$_5$N$_2$, forms yellow crystals, m. p. 166—167°; *aminoethyl-morphine*, obtained by reduction with stannous chloride, has m. p. 115—116°; *acetylaminoethylmorphine*, by reduction with tin and acetic acid, forms a pale yellow *hydrochloride*; and *diacetylaminoethyl-morphine*, C$_{23}$H$_{28}$O$_5$N$_2$, prepared by acetylating the amino-compound, has m. p. 156°.

All these substances give very similar reactions with formaldehyde-sulphuric acid, Froehde's and Erdmann's reagents.   J. C. W.

Action of Acylamino-acid Chlorides on Ethyl and Methyl Sodiomalonate and Ethyl Sodiocyanoacetate. II. ERNST PFAEHLER (*Ber.*, 1913, **46**, 1702—1716. Compare this vol., i, 622).— A mixture of a benzene solution of phthalylglycyl chloride with ethyl sodiomalonate (compare Gabriel and Colman, A., 1909, i, 491) gives a clear liquid from which during several days there separates the sodium derivative of *ethyl γ-phthalimino-β-ketopropanedicarboxylate*,

$$C_6H_4\!\!<^{CO}_{CO}\!\!>N\cdot CH_2\cdot CO\cdot CH(CO_2Et)_2,$$
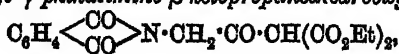
prisms, m. p. 68—68·5°; this ester with an alcoholic solution of sodium ethoxide yields needles of the *sodium* derivative, whilst it dissolves in aqueous ammonia solution shortly depositing the *ammonium* derivative, decomp. at 210°, m. p. 255—260°; it has an acid reaction, and gives a deep red coloration with ferric chloride in alcoholic solution; in chloroform solution it reacts with bromine, forming a *bromo*-derivative, $C_{17}H_{16}O_7NBr$, needles, m. p. 122—122·5°, whilst the corresponding *chloro*-compound forms needles, m. p. 95—96°. The sodium derivative when boiled with water and the solution acidified yields phthalylglycine, whilst the ketonic acid is decomposed by boiling with concentrated hydrochloric acid with the production of aminoacetone hydrochloride. When heated for six hours at 185° with benzyl chloride, the sodium derivative is converted into *ethyl γ-phthalimino-β-keto-a-benzylpropanedicarboxylate*,

$$C_6H_4{<}^{CO}_{CO}{>}N·CH_2·CO·C(CH_2Ph)(CO_2Et)_2,$$
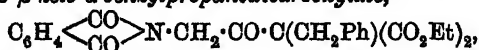
cubes, m. p. 98°. The free ester, ethyl phthalylglycylmalonate, when warmed with water at 100°, undergoes hydrolysis with subsequent loss of a molecule of carbon dioxide, giving rise to *ethyl γ-phthaliminoacetoacetate*, m. p. 110°; this gave a coloration with ferric chloride, but no metallic derivatives could be isolated ; the *aa-dibromo*-derivative,

$$C_6H_4{<}^{CO}_{CO}{>}N·CH_2·CO·CBr_2·CO_2Et,$$
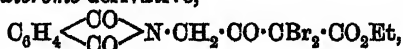
m. p. 87—88°, was obtained by direct substitution in chloroform solution.

Phthalylglycyl chloride in benzene solution readily reacts with a bimolecular proportion of ethyl sodiocyanoacetate ; the *sodium* derivative which separates, on treatment with hydrochloric acid, yields the free *ethyl γ-phthalimino-a-cyano-β-keto-n-butyrate*,

$$C_6H_4{<}^{CO}_{CO}{>}NH·CH_2·CO·CH(CN)·CO_2Et,$$
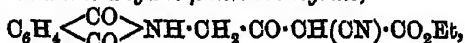
needles, m. p. 148—149°; on boiling with water, this substance undergoes considerable change, and after a few hours pure phthalic acid is obtained.

The clear liquid, obtained by mixing ethyl sodiomalonate and phthalyl-β-alanyl chloride in benzene slowly deposits the *sodium* derivative of *ethyl δ-phthalimino-β-ketobutanedicarboxylate*,

$$C_6H_4{<}^{CO}_{CO}{>}NH·CH_2·CH_2·CO·CH(CO_2Et)_2 ;$$
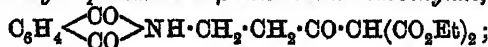
the free ester, needles, m. p. 68—69°, can be liberated by hydrochloric acid ; it is a strongly acidic substance, which with ferric chloride gives a red coloration, and when boiled with water yields ethyl δ-phthalimino-β-keto-*n*-valerate, m. p. 121—122°.

Phthalylphenylglycyl chloride, m. p. 141—143°, was prepared by treating the acid with phosphorus pentachloride ; its interaction with ethyl sodiomalonate yielded the *sodium* derivative of *ethyl γ-phthalimino-β-keto-γ-phenylpropanedicarboxylate*,

$$C_6H_4{<}^{CO}_{CO}{>}N·CHPh·CO·CH(CO_2Et)_2 ;$$
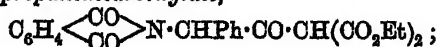
the free ester, leaflets and prisms, m. p. 104—105°, is acid in reaction,

and gives a red colour with ferric chloride ; when boiled with a mixture of concentrated hydrochloric acid and acetic acid it undergoes scission, producing α-aminobenzyl methyl ketone.

α-Phthalimino-α-ethyl-n-butyryl chloride and ethyl sodiomalonate give as reaction product the yellow *sodium* salt of *ethyl γ-phthalimino-β-keto-γ-ethyl-n-pentanedicarboxylate,*

$$C_6H_4\!<^{CO}_{CO}\!\!>\!N\cdot CEt_2\cdot CO\cdot CH\cdot(CO_2Et)_2 \; ;$$
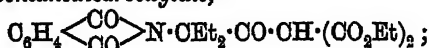
the free ester, prisms, m. p. 72—73°, gives the ferric chloride reaction, but is not appreciably acidic ; unlike the esters described above, when warmed with sodium ethoxide, it undergoes rearrangement, yielding an acid *substance*, which from analogy with the corresponding *gem*-dimethyl compound (Pfaehler, *loc. cit.*) is probably a pyrrolidone derivative of the structure $CO_2Et\cdot C_6H_4\cdot CO\cdot N\!<^{CO-CH\cdot CO_2Et}_{CEt_2\cdot CO}$. In the original preparation, involving the acid chloride and ethyl sodiomalonate, the sodium derivative produced is accompanied by a substance, cubical crystals, m. p. 229—230°, insoluble in water, which proves to be *α-phthalimino-α-ethyl-n-butyric anhydride,* a remarkably stable substance, which is not affected by phosphorus pentachloride or boiling water or alcohol. Another by-product occurring in smaller quantity is *ethyl benzoylenediethylpyrrolonecarboxylate,* $^{C_6H_4\cdot C:C(CO_2Et)}_{CO-N-CEt_2}\!\!>\!CO$, a lemon-yellow substance, m. p. 85—85·5°, which is obtained in larger quantity if the reaction mixture is kept for a longer time under benzene containing an additional quantity of ethyl sodiomalonate. The normal ester, m. p. 72—73°, when boiled for thirty minutes with hydriodic acid (b. p. 127°) undergoes scission, yielding *methyl α-amino-α-ethyl-n-propyl ketone hydriodide,* short, columnar crystals, m. p. 184—186° ; *hydrochloride,* silky needles, m. p. 236—236·5° ; *platinichloride,* lemon-yellow needles, m. p. 188° (decomp.) ; *picrate,* yellow needles, m. p. 166° ; *benzoyl* derivative, needles, m. p. 80—81° ; the free base has an odour resembling that of turpentine.

Methyl sodiomalonate behaves like the corresponding ethyl compound towards phthaliminoethylbutyryl chloride, producing as by-product the same acid anhydride as mentioned above, together with the *sodium* derivative of *methyl γ-phthalimino-β-keto-γ-ethyl-n-pentanedicarboxylate* as main product ; the free ester, prisms, m. p. 97—98°, is neutral, but gives the ferric chloride reaction ; with sodium ethoxide it shows the same behaviour as the ethyl ester, whilst its sodium derivative when heated with methyl iodide in acetone solution is converted into *methyl δ-phthalimino-γ-keto-γ-ethyl-n-hexane-$\beta\beta$-dicarboxylate,*

$$C_6H_4\!<^{CO}_{CO}\!\!>\!N\cdot CEt_2\cdot CO\cdot CMe(CO_2Me)_2,$$
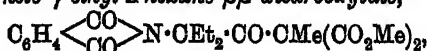
needles, m. p. 113—114°, which gives no ferric chloride reaction. Again, like the ethyl ester, the methyl ester in benzene solution is converted by the action of methyl sodiomalonate into *methyl benzoylenediethylpyrrolonecarboxylate,* lemon-yellow needles, m. p. 109—110° ; this and also the corresponding ethyl ester are converted by hydrobromic acid into

diethylpy rrolonebenzo acid hydrobromide, yellow cubes, m. p. 214° (decomp.), which by the action of water or alkali yields *diethyl-pyrrolonebenzoic acid,* $\mathrm{CO-CH}^{\mathrm{CEt_2 \cdot NH}} > \mathrm{C \cdot C_6H_4 \cdot CO_2H}$, prisms and leaflets, m. p. 184·5—185° (decomp.); this on heating to 200° passes into the corresponding *lactam (benzoylenediethylpy rrolone),* $\mathrm{CO-N-CEt_2}^{\mathrm{C_6H_4 \cdot C=CH}} > \mathrm{CO}$, colourless needles, m. p. 71°.

a-Phthalimino-a-methyl-*n*-butyryl chloride in a similar manner with ethyl sodiomalonate gives the corresponding *phthaliminomethylbutyric anhydride,* cubes, m. p. 183°, insoluble in water, together with the expected sodium derivative, from which carbon dioxide liberates *ethyl γ-phthalimino-β-keto-γ-methyl-n-pentanedicarboxylate,*

$$\mathrm{C_6H_4}{<}^{\mathrm{CO}}_{\mathrm{CO}}{>}\mathrm{N \cdot CMeEt \cdot CO \cdot CH \cdot (CO_2Et)_2} \ ;$$
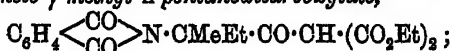
this is a neutral oil which gives an intense coloration with ferric chloride. When this substance is heated in alcoholic solution with sodium ethoxide, or its sodium derivative heated in alcohol, a soluble sodium salt is produced, from which hydrochloric acid frees an isomeric *pyrrolidine derivative,* $\mathrm{CO-CMeEt}^{\mathrm{CH(CO_2Et) \cdot CO}} > \mathrm{N \cdot CO \cdot C_6H_4 \cdot CO_2Et}$, m. p. 110°, which on heating with dilute acid is converted into *carbethoxybenzoyl-methylethyltetramic acid* [*ethyl 3 : 5-diketo-1-benzoyl-2-methyl-2-ethylpyr rolidine-o-carboxylate*], $\mathrm{CO \cdot CMeEt}^{\mathrm{CH_2-CO}} > \mathrm{N \cdot CO \cdot C_6H_4 \cdot CO_2Et}$, an acidic substance, m. p. 186—187°. The application of sodium methoxide to the same oily ethyl ester, or of methyl alcohol to its sodium derivative in a similar manner, causes a replacement of ethyl by methyl, the pyrrolidine *derivative,* prisms, m. p. 139—140°, produced being of the structure $\mathrm{CO-CMeEt}^{\mathrm{CH(CO_2Et) \cdot CO}} > \mathrm{N \cdot CO \cdot C_6H_4 \cdot CO_2Me}$; the acidity of this substance is sufficient to cause its aqueous solution when heated to eliminate the carbethoxy-group with formation of *methyl 3 : 5-diketo-1-benzoyl-2-methyl-2-ethylpyrrolidine-o-carboxylate,*

$$\mathrm{CO-CMeEt}^{\mathrm{CH_2-CO}} > \mathrm{N \cdot CO \cdot C_6H_4 \cdot CO_2Me},$$
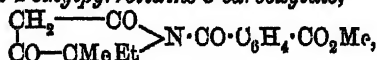
m. p. 209°, which reacts with bromine in chloroform solution, giving a neutral *dibromo*-derivative, m. p. 166—167°, by displacement of the methylene hydrogen atoms in the ring.

a-Phthalimino-a-methyl-*n*-butyryl chloride reacts with methyl sodiomalonate, yielding needles or prisms of *methyl γ-phthalimino-β-keto-γ-methyl-n-pentanedicarboxylate,* m. p. 98—99°, which colours ferric chloride blood-red. This substance with sodium ethoxide undergoes rearrangement into a pyrrolidine *compound,*

$$\mathrm{CO-CMeEt}^{\mathrm{CH(CO_2Me) \cdot CO}} > \mathrm{N \cdot CO \cdot C_6H_4 \cdot CO_2Et},$$
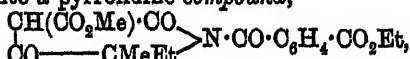
needles, m. p. 108—109ᵛ (of which an isomeride, m. p. 139—140°, has been described above), which when boiled with water yields the

pyrrolidine derivative, m. p. 186—187°, described earlier. Sodium methoxide on the other hand yields a *compound*,

$$\begin{array}{c} CH(CO_2Me)\cdot CO \\ CO\text{-----}CMeEt \end{array}\!\!>\!N\cdot CO\cdot C_6H_4\cdot CO_2Me,$$
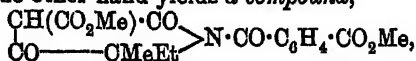
prisms, m. p. 146—147°, which is more acid in character than acetic acid, and which easily loses the carbomethoxy-group, producing the pyrrolidine derivative, m. p. 209°.

The action of ethyl sodiocyanoacetate on α-phthalimino-α-methyl-*n*-butyryl chloride gives a yellow *sodium* derivative, from which acetic acid liberates *ethyl γ-phthalimino-α-cyano-β-keto-γ-methyl-n-hexoate*,

$$C_6H_4\!\!<\!\!\begin{array}{c} CO \\ CO \end{array}\!\!>\!N\cdot CMeEt\cdot CO\cdot CH(CN)\cdot CO_2Et,$$
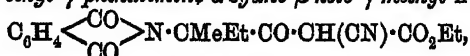
m. p. 140°; this loses carbon dioxide when boiled with water, but the decomposition is not a simple one.

The pyrrolone condensation observed with phthaliminoethyl-*n*-butyryl chloride and excess of ethyl or methyl sodiomalonate occurs under the same conditions with the phthaliminomethylbutyryl compounds. *Methyl benzoylenemethylethylpyrrolonecarboxylate*,

$$\begin{array}{c} C_6H_4\cdot C\!=\!C(CO_2Me) \\ CO\text{---}N\text{-----}CMeEt \end{array}\!\!>\!CO,$$

forms yellow prisms, m. p. 130—131°; the corresponding yellow *ethyl* ester forms prisms, m. p. 112°. Both these esters react with hydrobromic acid, D 1·48, producing *methylethylpyrrolonebenzoic acid hydrobromide*, yellow needles, from which alkali in theoretical quantity separates the free *acid*,

$$\begin{array}{c} CO\text{-----}OH \\ CMeEt\cdot NH \end{array}\!\!>\!C\cdot C_6H_4\cdot CO_2H,\ \text{prisms,}$$

m. p. 177° (decomp.), which above its m. p. passes into *benzoylenemethylethylpyrrolone*,

$$\begin{array}{c} C_6H_4\cdot C\!=\!CH \\ CO\text{---}N\cdot CMeEt \end{array}\!\!>\!CO,\ \text{needles, m. p. 94—95°.}$$

If methyl γ-phthalimino-β-keto-γ-methyl-*n*-pentanedicarboxylate is submitted to the action of methyl iodide in boiling acetone solution it is methylated to *methyl δ-phthalimino-γ-ketomethyl-n-hexane-ββ-dicarboxylate*, $C_6H_4\!\!<\!\!\begin{array}{c} CO \\ CO \end{array}\!\!>\!N\cdot CMeEt\cdot CO\cdot CMe(CO_2Me)_2,$ prisms, m. p.

104°; this substance, which gives no ferric chloride reaction, is converted by boiling hydrochloric acid into oily *γ-amino-γ-methylhexan-δ-one*,

$$NH_2\cdot CMeEt\cdot COEt,$$

hydrochloride, crystalline; *picrate*, leaflets, m. p. 147—148°.　D. F. T.

3-Nitropyridine and some of its Reduction Products. FRANZ FRIEDL (*Monatsh.*, 1913, **34**, 759—767).—The nitration of pyridine (A., 1912, i, 299) is most conveniently effected by the gradual addition of a solution of potassium nitrate in nitric acid (D 1·5) to a mixture of pyridine with an excess of sulphuric acid at 290—300°. It has already been shown that the product, 3-nitropyridine, is convertible by energetic reduction in acid solution into 3-aminopyridine, but it is now found that the analogy to nitrobenzene is still greater, extending to the successive formation of an azoxy-, azo-, and hydrazo-derivative when reduced in alkaline media.

3-Nitropyridine forms colourless needles, m. p. 41°, b. p. 216°;

hydrochloride, colourless leaflets, m. p. 154°; *sulphate*, hygroscopic crystals; *aurichloride*, yellow needles, m. p. 140°, *platinichloride*, broad, yellow needles, decomp. at 254°; *argentonitrate*,

$$(C_5H_4O_2N_2)_2,AgNO_3,$$
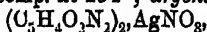
colourless needles, m. p. 175—176°.

When 3-nitropyridine is treated with a boiling solution of arsenious oxide in aqueous sodium hydroxide under reflux, it is reduced almost quantitatively to the corresponding *azoxypyridine*, silky needles, m. p. 130—131°, to a yellow liquid, which can be further reduced by zinc dust and alcoholic sodium hydroxide to *azopyridine*, orange-red needles, m. p. 142°, the yield again being almost the theoretical. The application of sodium methoxide as reducing agent for the production of the azoxy-compound and of iron filings for the azo-compound is unsatisfactory, yielding a complex mixture in each case and consequently an impure product.

If azopyridine is treated with zinc dust and boiling aqueous alcoholic sodium hydroxide in an atmosphere of hydrogen, reduction occurs with the formation of an 80% yield of *hydrazopyridine*, colourless needles, m. p. 202°; the pure substance is stable, but in alkaline alcoholic solution it undergoes atmospheric oxidation, especially readily on warming, with the production of azopyridine. It was not found possible to reduce hydrazobenzene further.

Partial nitration of pyridine occurs when nitric acid vapour is led into boiling pyridine nitrate, but there are formed simultaneously with 3-nitropyridine, also three other basic substances, m. p. 80°, 120, and 258° respectively; oxides of nitrogen in place of nitric acid lead to a similar result. Pyridine sulphate likewise gives a little 3-nitropyridine, but the main portion of the product consists of an oily mixture, b. p. 240—300°, of basic nature, from which could be isolated a *base*, woolly needles, m. p. 110°; *nitrate*, m. p. 245°; the base is very resistant to oxidising and reducing agents, and it is possibly related to the polymerised nitropyridine obtained by Spencer (P., 1903, **19**, 79).

D. F. T.

Syntheses of the Indole Group. IV. Basic Properties of Indoles, and Polymerides of Indoles. BERNARDO ODDO (*Gazzetta*, 1913, **43**, i, 385—394. Compare A., 1912, i, 649).—The publication of the author's results on polymeric indoles has been anticipated to some extent by that of Keller (this vol., i, 403). Di-indole hydrochloride (compare Keller, *loc. cit.*) is a microcrystalline powder, m. p. 180°, forming a yellow liquid. It can be prepared by the prolonged action of dilute aqueous hydrochloric acid on indole at the ordinary temperature, or by treating indole with concentrated hydrochloric acid for a few minutes, as well as by the action of hydrogen chloride on an anhydrous ethereal solution of indole.

a-Methylindole hydrochloride, C_9H_9N,HCl, may be obtained by the action of hydrogen chloride on an anhydrous ethereal solution of a-methylindole.

The author gives also the results of some preliminary experiments regarding the power of indoles to form simple or double salts.

R. V. S.

Condensation of Primary and Secondary Aromatic Amines with Mesoxalic Esters. Synthesis in the Indole Series. ALFRED GUYOT and J MARTINET (*Compt. rend.*, 1913, **156**, 1625—1628).—Schmitt (A., 1905, i, 585) and Curtiss, Hill and Lewis (A., 1911, i, 366) obtained anilino-derivatives of the type $NHPh \cdot C(CO_2R)_2 \cdot OH$; $NPh:C(CO_2R)_2$; $NHPh \cdot C(CO_2R)_2 \cdot NHPh$ by the interaction of aromatic amines with mesoxalic esters. The authors have, however, obtained, as principal product of such reactions an ester of dioxindole-3-carboxylic acid (annexed formula), which is saponified by aqueous potassium hydroxide in the absence of air, giving the corresponding dioxindole, carbon dioxide being eliminated. In an open vessel oxygen is rapidly absorbed, and the product formed is the corresponding isatin. The amine is warmed with the mesoxalic ester in acetic acid solution at 60° for one hour, and then the acid and residual amine are removed by steam. From the product any phenyltartronic acid produced is extracted with hydrochloric acid, and the residual indole derivative is crystallised from ether.
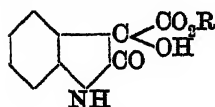
From *p*-toluidine the authors have prepared *methyl 5-methyldioxindole-3-carboxylate*, m. p. 251°, the *ethyl* ester, m. p. 212°, 5-*methyldioxindole*, m. p. 210°, and the corresponding isatin.

From β-naphthylamine, *methyl 3-hydroxy-2-ketodihydro-ββ-naphthindole-3-carboxylate*, m. p. above 300°, the *ethyl* ester, m. p. 210°, and the corresponding dioxindole and isatin.

From methylaniline, *methyl 1-methyldioxindole-3-carboxylate*, m. p. 217°, the *ethyl* ester, m. p. 130°, *methyl p methylaminophenyltartronate*, m. p. 85°, and the dioxindole and isatin.

From ethylaniline, *ethyl 1-ethyldioxindole-3-carboxylate*, m. p. 141°, *ethyl p-ethylaminophenyltartronate*, m. p. 65°, the dioxindole, and isatin.

From ethyl-β-naphthylamine, *ethyl 2-hydroxy-3-keto-1-ethyldihydro-ββ-naphthindole-3-carboxylate*, m. p. 181°, the *dioxindole*, m. p. 172°, and the *isatin*, fine red needles, m. p. 173°.

From tetrahydroquinoline, *methyl 1:7-trimethylenedioxindole-3-carboxylate* (formula I), m. p. 188°, the *ethyl* ester, m. p. 174°, 1:7-*trimethylenedioxindole* (formula II), m. p. 160°, and 1:7-*trimethyleneisatin* (formula III), deep red prisms, m. p. 195°.
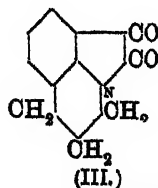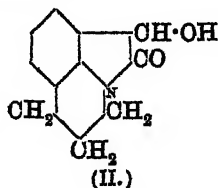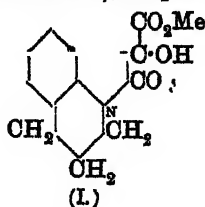
W. G.

1-Methylisatins. MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1913, **34**, 787—794).—In the preparation of 1-methylisatin from isatin there is no necessity to isolate the intermediate

sodium derivative of isatin (compare Heller, A., 1907, i, 442), and the subsequent reaction with methyl iodide in a sealed tube can also be avoided. If isatin is treated with the calculated quantity of 25% methyl-alcoholic potassium hydroxide, the separation of the blue potassium derivative gives rise to a paste which on the addition of methyl sulphate (under reflux) enters into reaction so vigorously that the mixture boils; 1-methylisatin can be easily separated from the reaction mixture (compare Friedländer and Kielbasinski, A., 1911, i, 1021).

Following a similar course 5-bromoisatin can be converted into 5-*bromo*-1-*methylisatin*, red, microscopic needles, m. p. indistinct at 164°, and 5 : 7-dibromoisatin into 5 : 7-*dibromo*-1-*methylisatin*, red, microscopic needles, m. p. indistinct at 171°. In these cases the sodium compounds react less vigorously with methyl sulphate than does the sodium compound of the unsubstituted isatin.

If carefully dried methylisatin is treated in boiling acetic anhydride containing a little acetic acid, with small quantities of zinc dust until decolorisation is complete, diacetyl-1 : 1'-dimethylisatyd,

$$NMe\left\langle{}^{C_6H_4}_{CO}\right\rangle{}O(OAc)\cdot C(OAc)\left\langle{}^{C_6H_4}_{CO}\right\rangle{}NMe,$$
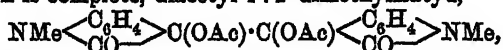
colourless, rhombohedral crystals, m. p. 218—220°, is obtained.

1-Methylisatin reacts with magnesium phenyl bromide in ethereal solution, giving a yellow, microcrystalline *substance*, $C_{21}H_{17}ON$, m. p. 145°; this is probably of the structure $^{C_6H_4\cdot CPh}_{NMe-CPh}\!\!>\!\!O$, produced by elimination of the elements of water from the ditertiary alcohol first formed by the action of the Grignard reagent on the two ketonic groups. **D. F. T.**

Some Derivatives of *cyclo*Hexanone and the Three Methyl-*cyclo*hexanones. VINCENZO SQUINTANI (*Atti R. Accad. Sci. Torino*, 1912–13, **48**, 675—686. Compare Guareschi, A., 1911, i, 792).—On warming a mixture of *cyclo*hexanone, ethyl cyanoacetate, and an alcoholic solution of methylamine, *aa'*-*dicyanocyclohexane*-1 : 1-*diaceto-methylimide*, $CH_2\left\langle{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}\right\rangle{}C\left\langle{}^{CH(CN)\cdot CO}_{CH(CN)\cdot CO}\right\rangle{}NMe$, is produced; it has m. p. 175°. Its aqueous solution, when neutralised by ammonia, gives a blue precipitate with copper sulphate and a white, flocculent precipitate with silver nitrate. When treated with bromine it yields a white, flocculent compound, probably the *dibromide*, and when this is boiled with 10% alcoholic formic acid, *aβ-dicyano-aβ-cyclohexane-succinomethylimide*, $CH_2\left\langle{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}\right\rangle{}C\left\langle{}^{C(CN)\cdot CO}_{C(CN)\cdot CO}\right\rangle{}NMe$, is formed; it is a white, crystalline substance, m. p. 222°.

When a mixture of 1-methyl*cyclo*hexan-4-one, ethyl cyanoacetate and alcoholic ammonia is kept for some hours, an ammoniacal salt is deposited; from this, by the action of dilute acid, the *imide* of *aa'-dicyano-1-methylcyclohexane-4 : 4-diacetic acid*,

$$CHMe\left\langle{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}\right\rangle{}C\left\langle{}^{CH(CN)\cdot CO}_{CH(CN)\cdot CO}\right\rangle{}NH,$$
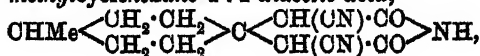
m. p. 210—211°, is obtained. Its *copper* salt is a chestnut-coloured precipitate which becomes yellowish-green ; when it is made anhydrous and heated, it assumes at about 120° a red tint, which disappears on cooling. The imide of m. p. 210—211° yields a *dibromo*-derivative, from which *αβ-dicyano-αβ-1-methylcyclohexane-4 : 4-succinimide*,

$$\text{CHMe} \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{C(CN)}\cdot\text{CO} \\ \text{C(CN)}\cdot\text{CO} \end{array} \text{NH},$$
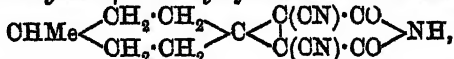
m. p. 207—208°, can be prepared.

αα'-Dicyano-1-methylcyclohexane-4 : 4-diacetomethylimide,

$$\text{CHMe} \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{CH(CN)}\cdot\text{CO} \\ \text{CH(CN)}\cdot\text{CO} \end{array} \text{NMe},$$
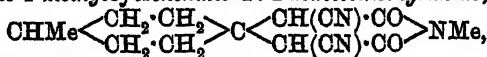
has m. p. 181—182°. It yields a crystalline *bromo*-derivative, m. p. 137°, which on treatment with an aqueous solution of sulphurous acid gives *αβ-dicyano-αβ-1-methylcyclohexane-4 : 4-succinomethylimide*,

$$\text{CHMe} \begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{C(CN)}\cdot\text{CO} \\ \text{C(CN)}\cdot\text{CO} \end{array} \text{NMe},$$
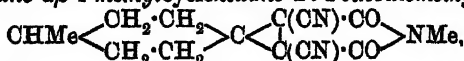
m. p. 182—183°.

1-Methyl*cyclo*hexan-2-one yields similar products.

The *ammonium* salt, $C_{13}H_{18}O_2N_4$, obtained from 1-methyl*cyclo*hexan-2-one, ethyl cyanoacetate, and alcoholic ammonia has m. p. 165°. The corresponding *αα'-dicyano-1-methylcyclohexane-2 : 2-diacetimide*,

$$\text{CH}_2 \begin{array}{c} \text{CH}_2\cdot\text{CHMe} \\ \text{CH}_2\text{---}\text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{CH(CN)}\cdot\text{CO} \\ \text{CH(CN)}\cdot\text{CO} \end{array} \text{NH},$$
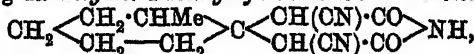
has m. p. 210°. Its *copper* salt is a rusty-red precipitate which turns bluish-green.

αβ-Dicyano-αβ-1-methylcyclohexane-2 : 2-succinimide,

$$\text{CH}_2 \begin{array}{c} \text{CH}_2\cdot\text{CHMe} \\ \text{CH}_2\text{---}\text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{C(CN)}\cdot\text{CO} \\ \text{C(CN)}\cdot\text{CO} \end{array} \text{NH},$$
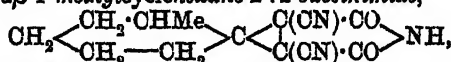
is a microcrystalline substance, m. p. 235—236°.

αα'-Dicyano-1-methylcyclohexane-2 : 2-diacetomethylimide,

$$\text{CH}_2 \begin{array}{c} \text{CH}_2\cdot\text{CHMe} \\ \text{CH}_2\text{---}\text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{CH(CN)}\cdot\text{CO} \\ \text{CH(CN)}\cdot\text{CO} \end{array} \text{NMe},$$
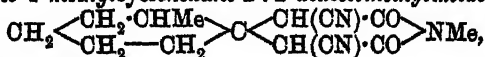
has m. p. 181—182°.

αα'-Dicyano-1-methylcyclohexane-3 : 3-diacetomethylimide,

$$\text{CH}_2 \begin{array}{c} \text{CHMe}\cdot\text{CH}_2 \\ \text{CH}_2\text{---}\text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{CH(CN)}\cdot\text{CO} \\ \text{CH(CN)}\cdot\text{CO} \end{array} \text{NMe},$$
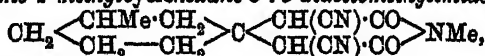
has m. p. 154°; in its preparation, a *substance* of m. p. 195—198° is also met with.   R. V. S.

Preparation of Nitro-*N*-alkylcarbazoles. FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 259504).—The nitration of *N*-alkylcarbazoles has previously given rise to a mixture of difficultly separable nitro-derivatives, but it is now found that if nitrous acid is employed definite compounds are obtained.

Nitro-9-ethylcarbazole, yellow crystals, m. p. 128°, is obtained when 9-ethylcarbazole (200 parts) in benzene (1000 parts) is mixed with a concentrated aqueous solution of sodium nitrite, and 600 parts of hydrochloric acid slowly added with efficient stirring at the ordinary temperature and the mixture subsequently boiled. *Nitro-9-methylcarbazole* forms small needles, m. p. 147—148°.   F. M. G. M.

Preparation of Arylanthraquinone Derivatives. FARBEN-
FABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 259037. Compare this
vol., i, 95—105).—4-p-*Toluidino*-1 : 2 *anthrathiazole*, dark blue needles,
is obtained by boiling 1-amino-4-p-toluidinoanthraquinone-2-
mercaptan with benzaldehyde (3 parts) and nitrobenzene (3 parts) ; on
sulphonation it furnishes a *compound* which dyes wool a fast violet
colour.

The analogous *compound* from 2-amino-1-p-toluidino-3-thioanthra-
quinone and benzaldehyde is obtained in brownish-violet prisms.

F. M. G. M.

Syntheses of Alkyloxymalachite-greens by means of
Magnesium Aryl Haloids. EMIL VOTOČEK and J. MATĚJKA (*Ber.*,
1913, 46, 1755—1759).—The present work has been undertaken with
the object of gaining insight into certain discrepancies observed in
condensations with tetramethyldiaminobenzhydrol (Votoček and
Jelínek, A., 1907, i, 245 ; Votoček and Krauz, A., 1909, i, 518).
The use of Grignard's reagents presents the advantage that operations
can be performed at a comparatively low temperature. A series of
alkyloxymalachite-greens has been prepared from the magnesium
derivatives of halogenated phenol ethers and Michler's ketone on the
one hand, and from methyl anisate and the magnesium derivative of
p-bromodimethylaniline on the other.

p-Methoxymalachite-green, obtained by the action of magnesium
p-anisyl bromide on an ethereal suspension of Michler's ketone and
subsequent decomposition of the product formed with hydrochloric acid
and reduction with sodium hyposulphite, has m. p. 106°, and is
identical with the compound prepared from anisaldehyde and dimethyl-
aniline. The same substance is formed when ethereal solutions of
magnesium p-dimethylaminophenyl bromide and methyl anisate (m. p.
46°, b. p. 255°) are mixed.

p-Ethoxymalachite-green is obtained in a similar manner from
magnesium p-phenetole bromide and Michler's ketone, and is identical
with the substance produced from p-ethoxybenzaldehyde and dimethyl-
aniline.

m-Methoxymalachite-green is prepared by the gradual addition of an
ethereal solution of magnesium m-methoxyphenyl iodide to a boiling
solution of Michler's ketone in benzene and subsequent reduction to
the leuco-base. It has m. p. 123°, and is identical with m-methoxy-
tetramethyldiaminotriphenylmethane prepared from m-methoxybenz-
aldehyde and dimethylaniline.

o-Methoxymalachite-green, prepared from magnesium o-methoxy-
phenyl iodide and Michler's ketone, is identical with the product
obtained from o-methoxybenzaldehyde and dimethylaniline. H. W.

Further Investigations of Alkyloxy-derivatives of Malachite-
Green. EMIL VOTOČEK and J. KOHLER (*Ber.*, 1913, 46, 1760—1769.
Compare A., 1907, i, 245 ; 1909, i, 518 ; also previous abstract).—A
difference has been previously noted between the leuco-bases obtained
from alkyloxybenzaldehydes and dimethylaniline, and those prepared

from tetramethyl-*p*-diaminobenzhydrol and phenolic ethers. This is now attributed to the transformation of the methoxy- into the hydroxy-group under the conditions of the experiments. The work has been further extended to ethoxy-derivatives and to polyhydroxy-phenols.

Tetraethyldiaminobenzhydrol is prepared by reduction of tetra-ethyldiaminobenzophenone by sodium and alcohol or by oxidation of *tetraethyldiaminodiphenylmethane*, m. p. 41°, with lead peroxide. It condenses with phenol in the presence of hydrochloric acid, forming p′-*hydroxy*-p″ : p‴-*tetraethyldiaminotriphenylmethane*, m. p. 110—111°, which is also obtained by heating *p*-hydroxybenzaldehyde and diethyl-aniline with hydrochloric acid and a little alcohol at 125° for twelve hours. When oxidised with chloranil, it gives a green dye which becomes violet on addition of alkali.

Tetraethyldiaminobenzhydrol does not react readily with anisole in the presence of hydrochloric acid, and does not yield a uniform product. On the other hand, anisaldehyde readily condenses with diethylaniline, yielding p′-*methoxy*-p″ : p‴-*tetraethyldiaminotriphenylmethane*, m. p. 65°. In the hope of obtaining an abnormal base of betaine-like structure (A., 1909, i, 519), the substance was heated with hydrochloric acid at 120° during two hours. The products of the action consisted of methyl chloride and *p*′-hydroxy-*p*″ : *p*‴ - tetraethyldiaminotriphenyl-methane. Since hydrochloric acid was found to have a similar action in the methoxy-series, the supposed existence of a larger number of isomerides is disproved, and the supposition of a betaine-like structure is rendered unnecessary.

p′-Hydroxy-*p*″ : *p*‴-tetramethyldiaminotriphenylmethane, m. p. 165°, is obtained from *p*-hydroxybenzaldehyde and dimethylaniline, and also from phenol and Michler's hydrol. The same substance is isolated with difficulty from the product of the action of hot concentrated hydro-chloric acid on a mixture of anisole and Michler's hydrol, the methyl group being partly eliminated during the reaction. That this is actually the case is proved by the isolation of the acetyl derivative of *p*′-hydroxy-*p*″:*p*‴-tetramethyldiaminotriphenylmethane, m. p. 145—146°, by the action of acetic anhydride on the above product, whereas, under the conditions employed, this reagent does not attack *p*′-methoxy-*p*″ : *p*‴-tetramethyldiaminotriphenylmethane. The latter substance evolves methyl chloride when heated with hydrochloric acid at 120°, and is converted into *p*′-hydroxy-*p*″ : *p*‴-tetramethyldiaminotriphenyl-methane. When the last-named substance is acted on by methyl sulphate, an impure product is obtained from which the hydroxy-compound can be regained after repeated crystallisation (compare A., 1909, i, 519).

Similarly, the compound obtained from Michler's hydrol and phenetole, and that from *p*-ethoxyleucomalachite-green and hydrochloric acid are shown to be *p*-hydroxyleucomalachite-green.

The methyl group is also completely eliminated from *m*-methoxy-leucomalachite-green by treatment with hydrochloric acid at 120° during two hours. *o*-Methoxyleucomalachite-green is not completely decomposed under these conditions.

p-*Dimethoxyleucomalachite-green*, m. p. 129—130°, is obtained by the addition of an ethereal solution of magnesium p-dimethoxyphenyl bromide to a solution of Michler's ketone in ether and benzene, and subsequent reduction of the dye formed by means of sodium hyposulphite, whilst the same substance can also be prepared by the condensation of Michler's hydrol and quinol dimethyl ether in the presence of hydrochloric acid and alcohol. When oxidised by chloranil, it yields a green dye, stable towards alkalis.

Michler's ketone may be condensed with catechol in the presence of phosphoryl chloride, and the dye produced is readily reduced to dihydroxytetramethyldiaminotriphenylmethane, m. p. 162—163°. The substance is identical with that obtained from protocatechualdehyde and dimethylaniline, or from catechol and Michler's hydrol. Under similar conditions, resorcinol yields a green *dye*, which becomes violet on addition of alkali; the corresponding leuco-base has not been obtained in the crystalline state. Quinol does not condense with Michler's ketone under these conditions.

The behaviour of these leuco-bases as photographic developers has been investigated. Reducing power is only observed in those cases in which the hydroxyl groups are in the ortho- or para-position.

H. W.

Influence of the Halogens on Phototropy in Hydrazones.

II. FERDINANDO GRAZIANI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 623—629. Compare A., 1910, i, 777).—The paper describes the hydrazones derived from the three isomeric chlorophenylhydrazines.

None of the o-compounds is phototropic, all the m-derivatives are phototropic, whilst four of the eight p-derivatives prepared are phototropic.

Benzaldehyde-o-chlorophenylhydrazone, $C_6H_4Cl\cdot NH\cdot N\colon CHPh$, crystallises in minute, colourless needles, m. p. 73°.

Anisaldehyde-o-chlorophenylhydrazone, $C_6H_4Cl\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot OMe$, is a white, crystalline powder, m. p. 67°.

Cuminaldehyde-o-chlorophenylhydrazone,
$C_6H_4Cl\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot CHMe_2$,
forms slightly yellow needles, m. p. 67°.

Cinnamaldehyde-o-chlorophenylhydrazone,
$C_6H_4Cl\cdot NH\cdot N\colon CH\cdot CH\colon CHPh$,
crystallises in flat, sulphur-yellow needles, m. p. 99°.

Piperonaldehyde-o-chlorophenylhydrazone,
$C_6H_4Cl\cdot NH\cdot N\colon CH\cdot C_6H_3\colon O_2\colon CH_2$,
forms slightly yellow, flat needles, m. p. 96°.

Anisaldehyde-m-chlorophenylhydrazone,
$C_6H_4Cl\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot OMe$,
crystallises in flat, colourless needles, m. p. 135°.

Cuminaldehyde-m-chlorophenylhydrazone,
$C_6H_4Cl\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot CHMe_2$,
forms flat, colourless needles, m. p. 131°, and is very phototropic.

Cinnamaldehyde-m-chlorophenylhydrazone,
$C_6H_4Cl\cdot NH\cdot N\colon CH\cdot CH\colon CHPh$,
is a yellow, crystalline powder, m. p. 120°.

Piperonaldehyde-m-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_3:O_2:CH_2,$$
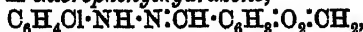
forms minute, colourless needles, m. p. 95°; it is very strongly phototropic.

Salicylaldehyde-*m*-chlorophenylhydrazone is very feebly phototropic.

p-*Tolualdehyde*-m-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_4\cdot Me,$$
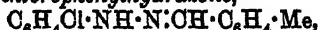
is a white, crystalline powder, m. p. 112°.

Benzaldehyde-*p* chlorophenylhydrazone has been prepared by Hewitt (T., 1893, **63**, 873), who gave m. p. 127°; the present author finds m. p. 132°. The substance is phototropic.

Anisaldehyde-p-*chlorophenylhydrazone*, $C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_4\cdot OMe$, forms colourless leaflets, m. p. 150°, and is not phototropic.

Cuminaldehyde-p-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_4\cdot CHMe_2,$$
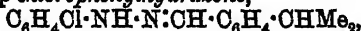
forms slightly yellow needles, m. p. 131°, and is very phototropic.

Cinnamaldehyde-p-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot CH:CHPb,$$

crystallises in yellowish-green needles, m. p. 136°; it is phototropic.

Piperonaldehyde-p-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_3:O_2:CH_2,$$
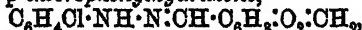
forms slightly yellow leaflets, m. p. 143°, and is not phototropic.

Salicylaldehyde-*p*-chlorophenylhydrazone has m. p. 173° (Auwers, A., 1909, i, 440, gave 169—170°). It is not phototropic.

p-*Tolualdehyde*-ɣ-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_4Me,$$
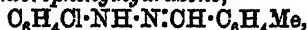
crystallises in slightly yellow needles, and is feebly phototropic.

Vanillin-p-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_3(OH)\cdot OMe,$$

forms flat, slightly yellow needles, m. p. 135°. It is not phototropic.

R. V. S.

The Formation of Dipiperidyls in the Electrolytic Reduction of Pyridine. BRUNO EMMERT (*Ber.*, 1913, **46**, 1716—1719).—From the formation of azobenzene and pinacone respectively in the reduction of nitrobenzene and acetone, and of phenylmethylpyrrolidone (Emmert, A., 1907, i, 339) in the reduction of a mixture of nitrobenzene and lævulic acid, it would appear that the first stage of the reduction is the production of free radicles which subsequently couple together. The electrolytic reduction of pyridine (Ahrens, A., 1897, i, 368), which has been believed to yield only piperidine, might therefore be expected to give rise to at least a small quantity of some binuclear product.

The reduction of pyridine at lead cathodes with a current density of 17·1 amps. per sq. dm. in diluted sulphuric acid is found to give actually much piperidine accompanied by less volatile products including 4 : 4′-dipiperidyl, m. p. 158—160°, 2 : 2′-dipiperidyl, b. p. 258—260° (corr.), and a high boiling resinous substance the molecule of which probably includes a higher number of piperidine nuclei; these less volatile products amounted to more than 10% of the pyridine taken.

D. F. T.

[Preparation of a Condensation Product from 5 : 7-Dichloro-isatin and 6-Chloroindoxyl.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 258258).—When a hot acetic acid solution of 5 : 7-dichloroisatin (220 parts) is treated with a similar solution of 6-chloroindoxyl (167 parts), some concentrated sulphuric acid added and the mixture warmed, it furnishes a *compound* crystallising in glistening, brown metallic needles. Differently substituted indoxyls and isatins can be employed for this reaction.   F. M. G. M.

Preparation of New Condensation Products from Indigotin and its Halogen Derivatives. GESELLSCHAFT FUR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 259145).—When indigotin derivatives are treated with aromatic acid haloids in the presence of a condensing agent, they furnish compounds which dye wool in yellow shades.

The *compound* obtained by the action of benzoyl chloride on indigotin in the presence of copper powder forms yellowish-green needles, m. p. 275—276°.   F. M. G. M.

Synthetic Bases Closely Related to the Cinchona Alkaloids. ADOLF KAUFMANN (*Ber.*, 1913, 46, 1823—1837).—The difference in toxicity between quinine and quinotoxine is not due to the rearrangement of the nitrogen in the quinuclidine ring into a secondary amino-group with a free hydrogen atom, for methylcinchotoxine is just as active as cinchotoxine. Experiments by A. Warschawski have now shown that 4-quinolyl ketone (A., 1912, i, 1017), although it is chemically related to quinotoxine, is antipyretic, and only very slightly poisonous, from which it appears that the ketone group is not responsible for the toxicity. On the other hand, the ethyl ester of meroquinenine and especially the reduction product, ethyl cincholeuponate, are very powerful poisons. However, the author maintains his former hypothesis (*ibid.*) that the specific action of quinine is connected with the presence of an adrenaline-like grouping, and has now prepared derivatives of the annexed type.
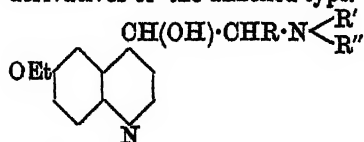
It was found that 6-alkyloxy-4-quinolyl ketones with methyl or methylene attached to the carbonyl group react with halogens, giving derivatives which condense with primary amines, and that the new substances could be reduced to hydroxy-compounds of the above type. They all have the same physiological effect as quinine, and give the same fluorescence and respond to the thalleoquinine test. The process is easily carried through, and it thus becomes possible to prepare numerous analogues of quinine.

I. [With MAX HUBER and A. STETTBACHER.]—The cinchotoxine obtained by boiling 10 grams of cinchonine hydrochloride with 400 c.c. of 0·001% hydrochloric acid for fifty hours was extremely small in amount (compare Biddle, A., 1912, i, 296), but was characterised as the *phenylhydrazone-picrate*, which separated in microscopic, red needles, m. p. 200°, when phenylhydrazine and picric acid were added

to the alkaline, ethereal extract. The reaction is sensitive in a dilution of 1 in 2500.

II. [With OTTO ZELLER and MAX HUBER.]—Meroquinenine was prepared by the hydrolysis of quinenine with 25% phosphoric acid at 180° (Koenigs, A., 1894, i, 392). The *p*-methoxylepidine *phosphate* separated on cooling in large, grey, lanceolate crystals, m. p. 208—210°, and the filtrate was fractionally precipitated with phosphotungstic acid. The meroquinenine obtained from the precipitate by means of baryta was esterified, and the hydrochloride Fof the ethyl ester (I) (Koenigs, A., 1906, i, 762), reduced by hydrogen and colloidal palladium to the hydrochloride of ethyl cincholeuponate, which formed beautiful white needles, m. p. 158°, $[a]_D^{20}$ +5·71° (compare Skraup, A., 1895, i, 484). The free *ester* (II) is a colourless liquid, b. p. 140°/ 14 mm., $[a]_D^{18}$ −17 2°, which reacts violently with methyl iodide, giving *ethyl* N-*methylcincholeuponate*, $C_{12}H_{23}O_2N$, as a colourless oil, b. p. 139°/21 mm.
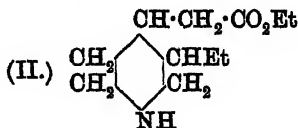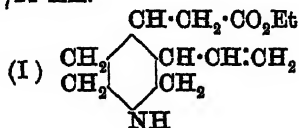
III. [With AUGUST POLL and HEINRICH PEYER.]—6-Ethoxy-4-quinolyl methyl ketone (this vol., i, 294) was warmed with bromine in hydrobromic acid, when the *hydrobromide* of 6-*ethoxy*-4-*quinolyl bromo-methyl ketone* separated in lemon-yellow crystals, m. p. 207°. The *hydrochloride*, m. p. 190°, crystallised when hydrochloric acid was used. The free *base* (III) forms yellow needles, m. p.104—105°, but is not so stable as the salts. When the hydrobromide is added to piperidine, diethylamine or dimethylamine in benzene or ether, the salt of the primary base is precipitated, and the new amino-ketone is obtained by evaporating the filtrate or by precipitation in the form of a salt.
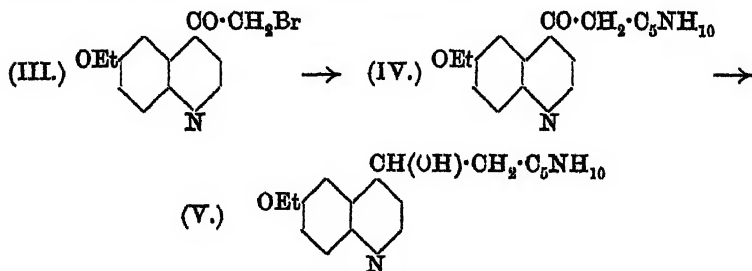
6-*Ethoxy*-4-*quinolyl piperidinomethyl ketone* (IV) crystallises in light yellow, sparkling leaflets, m. p. 158°, and the *hydrobromide* forms long, white needles, m. p. 189—190°. 6-*Ethoxy*-4-*quinolyl diethylamino-methyl ketone* (VI) is a yellow, crystalline powder, m. p. 131°, which yields a neutral *monobromide* in white needles and a yellow *dibromide*, m. p. 193—194°, which reacts acidic. The *dimethylamino-ketone*, $C_{15}H_{18}O_2N_2$, forms yellow, prismatic columns, m. p. 132°.

(VI.) → (VII.)
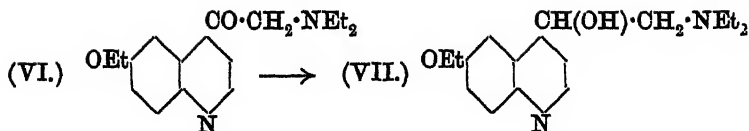
The ketones are readily reduced by hydrogen in presence of palladium. 6-*Ethoxy 4-β-piperidino-a-hydroxyethylquinoline* (V) crystallises in white needles and plates, m. p. 85°, and the 6-*ethoxy-4-β-diethylamino-a-hydroxyethylquinoline* (VII) forms a very soluble *hydrochloride* in soft, white needles, m. p. 171°. J. C. W.

Hydantoins. XXII. History of 2-Thiohydantoin. TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1913, **35**, 780—784).—2-Thiohydantoin was first synthesised by Klason (A., 1891, 179) by heating ethyl aminoacetate hydrochloride with potassium thiocyanate at 140—150°, but this work seems to have been overlooked by subsequent workers. Klason's observation has now been confirmed, but it has been found that the method gives too small a yield to be of practical value for preparing the compound. The reaction involves the intermediate formation of ethyl thiohydantoate. An attempt was therefore made to obtain 2-thiohydantoin by warming ethyl thiohydantoate with hydrochloric acid, but without success, hydrogen sulphide, ammonium chloride, and glycine hydrochloride being produced. E. G.

Preparation of ω-Methyl Sulphites [and ω-Alkyl Sulphites] of Substituted Aminoarylpyrazolones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D. R.-P. 259503—259577).—An account of the preparation of compounds previously described (this vol., i, 401), by the action of formaldehyde and sodium hydrogen sulphite on substituted aminopyrazolones. The second patent states that the formaldehyde can be replaced by other aldehydes, and describes the *compounds* obtained from 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone with acetaldehyde, and with propaldehyde, both of which have m. p. 124—125°, the latter decomposing at 130°. F. M. G. M.

Reactions of αβ-Diketonic Esters. ANDRÉ WAHL and M. DOLL (*Bull. Soc. chim.*, 1913, [iv], **13**, 468—485. Compare A., 1905, i, 474; 1907, i, 217; 1911, i, 108; 1912, i, 536, 625; this vol., i, 473).—The interaction of these esters with various reagents is described, and a number of the compounds obtained have been characterised. Some of this work has been recorded already (*loc. cit.*). The following observations and compounds are new :

Action of o-diamines (A., 1912, i, 536, 625).—*Ethyl 2-methylquinoxaline-3-carboxylate*, m. p. 74°, forms colourless needles. *Ethyl 2-methyl-1 : 4-naphthaquinoxaline-3-carboxylate*, m. p. 113—114°, forms slender, colourless needles. *Ethyl 2-propyl-1 : 4-naphthaquinoxaline-3-carboxylate*, m. p. 83—84°, crystallises in long, colourless needles. *Ethyl 2-n-butylquinoxaline-3-carboxylate* is an oil, but the corresponding acid, m. p. 86°, is crystalline. *Ethyl 2-phenylquinoxaline-3-carboxylate*,

m. p. 62—63°, forms silky needles; the *propyl* ester, m. p. 72—73°, and the iso*butyl* ester, m. p. 71°, are both crystalline. *Ethyl 2-phenyl-1 : 4-naphthaquinoxaline-3-carboxylate*, m. p. 116°, forms colourless needles.

Action of cyclic amines (A., 1912, i, 536, 625).—The aromatic esters condense with 2 mols. of the cyclic amines with the loss of $1H_2O$. The resulting compounds are probably best represented by the general formula $R \cdot CO \cdot C(NHPh)_2 \cdot CO_2Ph$ or

$$R \cdot C(:NPh) \cdot C(NHPh)(OH) \cdot CO_2Et.$$
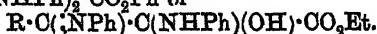
Methyl benzoylglyoxalate yields a *dianilide*, m. p. 144—145°, crystallising in yellow needles from warm benzene, and a *di*-p-*toluilide*, m. p. 115—116°, forming lemon-yellow crystals. The propyl ester gives a *dianilide*, m. p. 88—89°, and the *iso*butyl ester a *dianilide*, m. p. 108—109°.

Action of hydroxylamine (A., 1907, i, 217; 1912, i, 536, 626).—With the exception of ethyl acetylglyoxalate, which yields a dioxime, all the esters yield monoximes when treated with hydroxylamine; thus methyl *p*-methoxybenzoylglyoxalate furnishes methyl oximinoanisoylacetate (this vol., i, 214, 532).

Action of phenylhydrazine (A., 1905, i, 474; 1912, i, 213, 536, 626; this vol., i, 532).—Ethyl *n*-valeroylglyoxalate yields *4-phenylhydrazino-1-phenyl-3-n-butyl-5-pyrazolone*, m. p. 119—120°, crystallising in orange needles. Methyl anisoylglyoxalate in addition to the two compounds already described (A., 1912, i, 626) when boiled in acetic acid with 2 mols. phenylhydrazine yields 4-phenylhydrazino-1-phenyl-3-*p*-methoxyphenyl-5-pyrazolone (A., 1912, i, 213). Methyl benzoylglyoxalate may yield (1) the *additive product*, $COPh \cdot C(OH)(NH \cdot NHPh) \cdot CO_2Me$, m. p. 144—145°, or (2) a mixture of phenylhydrazinopyrazolone with the *monophenylhydrazone*, m. p. 76° (identical with methyl benzeneazobenzoylacetate) depending on the conditions of the reaction. iso*Butyl benzoylglyoxalatephenylhydrazone*, m. p. 62—63°, forms hexagonal tablets. Unlike phenylhydrazine, *p*-nitrophenylhydrazine does not give rise to additive products, but yields either α-mono-*p*-nitrophenylhydrazones or *p*-nitrophenylhydrazinopyrazolones (*loc. cit.*).

Action of semicarbazide (A., 1907, i, 217; 1912, i, 536, 626).—The acyclic esters yield normal disemicarbazones, whilst the cyclic esters furnish compounds which have the composition of disemicarbazones with 1 mol. H_2O in addition. Probably 1 mol. of semicarbazide is added to the α-carbonyl, whilst the second condenses normally with the β-carbonyl group. Methyl benzoylglyoxalate yields a *compound*, m. p. 215°, of this type, which on recrystallisation is partly converted into a yellow *compound*, m. p. 292°, which may be a true disemicarbazone.

Action of hydrazine hydrate (A., 1912, i, 536, 626; this vol., i, 532).—Ethyl valeroylglyoxalate yields *dibutyl-3 : 3'-rubazonic acid*, and ethyl hexoylglyoxalate gives *dihexyl-3 : 3'-rubazonic acid*. With cyclic esters additive products are formed consisting of 2 mols. of the ester and one of hydrazine hydrate when the reaction takes place in acetic acid. Such a product has been described for methyl anisoylglyoxalate, $N_2H_2[C(OH)(CO \cdot C_6H_4 \cdot OMe) \cdot CO_2Me]_2$ (A., 1912, i, 626); that yielded by methyl benzoylglyoxalate has m. p. 137°, and crystallises in yellow

spangles. In alcoholic solution the benzoylglyoxalates yield 3 : 3'-diphenylrubazonic acid (*loc. cit.*).

The benzoylglyoxalates condense with the benzoylacetates in presence of piperidine, forming compounds in which condensation has probably been effected by interaction of the β-ketonic ester with the α-carbonyl. The following *products* of this kind are described; they crystallise in colourless needles : methyl benzoylacetate with methyl benzoylglyoxalate, $CO_2Me \cdot CBz(OH) \cdot CHBz \cdot CO_2Me$ (?), m. p. 120°; ethyl benzoylacetate with methyl benzoylglyoxalate, m. p. 117—118°; methyl benzoylacetate with ethyl benzoylglyoxalate, m. p. 124—125°; methyl o-methoxybenzoylacetate with methyl benzoylglyoxalate, m. p. 136—137° (compare A., 1907, i, 217). T. A. H.

Behaviour of Diphenyltriketone with Amino-compounds. I. CARLO GASTALDI and F. CHERCHI (*Gazzetta*, 1913, **43**, i, 299—303).—When alcoholic solutions of diphenyltriketone and o-phenylenediamine are mixed and cooled, *benzoylphenylquinoxaline*,

$$\begin{array}{c} CPh\text{———}C\cdot COPh \\ N\cdot C_6H_4\cdot N \end{array}$$

separates in slightly yellow scales, m. p. 153°. Its constitution follows from the fact that it can also be obtained from bromodibenzoylcarbinyl acetate. When the solution from which the crystals of m. p. 153° separate is diluted with water, *diphenyltriketone o-phenylenediamine*, $COPh \cdot C(OH)_2 \cdot CPh:N \cdot C_6H_4 \cdot NH_2$, is obtained in colourless rosettes, m. p. 155°. When this compound is heated on the water-bath for ten hours in aqueous-alcoholic solution with hydrochloric acid, phenylbenziminazole hydrochloride, m. p. 343°, is produced. The phenylbenziminazole liberated from it has m. p. 294° (compare Japp and Meldrum, T., 1890, **57**, 1043). R. V. S.

Tetramethylpyrrindoquinone and Some Other Derivatives of 2 : 3-Dimethylpyrrole. OSCAR PILOTY and K. WILKE (*Ber.*, 1913, **46**, 1597—1603. Compare Piloty, A., 1910, i, 277).—The paper deals with the preparation of a quinone, tetramethylpyrrindoquinone, from 2 : 3-dimethylpyrrole-4-carboxylic acid. The authors have also prepared 2 : 3-dimethyl-1-ethylpyrrole for comparison with their "hæmopyrrole-*e*," but have not yet been able to prepare "hæmopyrrole-*e*" picrate from it. They have found further that trisubstituted *C*-derivatives of pyrrole can yield bispyrrole picrates, so that the power to form bispyrrole derivatives and their picrates does not seem to follow any law.

The preparation of 4-ethyl hydrogen 2 : 3-dimethylpyrrole-4 : 5-dicarboxylate (A., 1912, i, 899) is simplified by using the tin double salt of β-aminobutan-γ-one, instead of that substance itself. The employment of ethyl hydrogen oxalacetate, instead of ethyl oxalacetate, presents no advantage, but it leads to the formation of a by-product, termed *aphaninester acid*, probably of the
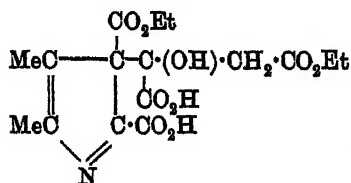
$$\begin{array}{c} CO_2Et \\ | \\ MeC\text{———}C\text{-}C\cdot(OH)\cdot CH_2\cdot CO_2Et \\ \| \quad\quad | \quad CO_2H \\ MeC \quad C\cdot CO_2H \\ \diagdown\diagup \\ N \end{array}$$

annexed formula. This substance crystallises in hair-like needles, m. p. 156°. *Tetramethylpyrrindoquinone* (annexed formula) is obtained by boiling 2 : 3-dimethylpyrrole-4-carboxylic acid (*loc. cit.*) with acetic anhydride for several hours; it crystallises in rhombic tablets, which are yellow by transmitted, red by reflected, light; at a high temperature the substance sublimes.
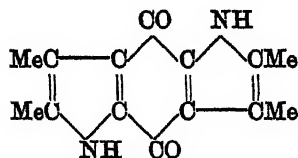
$$CO \quad NH$$
$$MeC—C \diagdown \diagup C \diagdown OMe$$
$$MeC \diagup C—C \diagup—OMe$$
$$NH \quad CO$$

2 : 3-*Dimethyl*-1-*ethylpyrrole*-4-*carboxylic acid*, $C_9H_{13}O_2N$, is obtained by acting on 4-ethyl potassium 2 : 3-dimethylpyrrole-4 : 5-dicarboxylate (*loc. cit.*) with ethyl sulphate in benzene solution, and saponifying the ester by means of boiling concentrated aqueous alkali; it forms thin rods, m. p. 156°. When compressed tablets of this acid are subjected to dry distillation, 2 : 3-*dimethyl*-1-*ethylpyrrole*, $C_8H_{13}N$, b. p. 59°/11 mm., is produced. If hydrogen chloride is passed into a dry ethereal solution of the substance, the bis-compound is obtained; it crystallises in a freezing mixture in long needles which melt at room-temperature.

Ethyl 1 : 2 : 3-*trimethylpyrrole*-4-*carboxylate*, $C_{10}H_{15}O_2N$ (prepared similarly, using methyl sulphate), forms flat, rhombic prisms, m. p. 52°. The *acid*, $C_8H_{11}O_2N$, forms stellar aggregates of small crystals, m. p. 229° (previously sintering and becoming slightly brown).

Ethyl 2 : 3-*dimethylpyrrole*-4 : 5-*dicarboxylate*, $C_{12}H_{17}O_4N$ (prepared by the action of ethyl sulphate on the potassium salt), forms rhombic leaflets, m. p. 110°. Its *picrate*, $C_{18}H_{20}O_{11}N_4$, crystallises in bright orange rods, m. p. 112—113°. The *picrate* of the methyl ethyl ester of the same acid (*loc. cit.*) forms straw-yellow needles, which sinter at 122°, and are completely melted at 140°; analysis gave the formula $C_{28}H_{38}O_{15}N_5$, indicating a bis-compound.

2 : 3-Dimethylpyrrole-4-carboxylic acid yields a *picrate*, $C_{20}H_{21}O_{11}N_5$, which forms compact, red rods, m. p. 143°.   R. V. S.

Existence of Phenyldi-imide. STEFAN GOLDSCHMIDT (*Ber.*, 1913 **46**, 1529—1532. Compare Vaubel, A., 1900, i, 522; this vol., i, 519 ;' Forster and Withers, T., 1913, **103**, 266).—Vaubel's supposed phenyldi-imide has been characterised by Forster and Withers as a mixture of aniline and phenylazoimide. The author has repeated Vaubel's experiments, and, employing conditions somewhat different from those used by Forster and Withers, finds that the product is pure phenylazoimide, b. p. 65—68°/12 mm., the identity of which is confirmed by the formation of a condensation product, m. p. 178—179°, with phenylacetonitrile (compare Dimroth, A., 1903, i, 129).

The author has further attempted to prepare di-imines by the oxidation of phenylhydrazine and *p*-bromophenylhydrazine. At the ordinary temperature, the action of oxidising agents, such as lead peroxide, silver oxide, or *p*-benzoquinone, etc., is accompanied by the evolution of nitrogen. Since the action of all these agents with the exception of *p*-benzoquinone ceases at 0°, the latter substance has alone been used.

When an ethereal solution of *p*-benzoquinone is gradually added to a

solution of *p*-bromophenylhydrazine in ether cooled to −60° with careful exclusion of moisture and carbon dioxide, a copious separation of quinhydrone occurs and a yellow filtrate is obtained from which nitrogen is evolved on warming. Addition of a solution of stannous chloride in ether causes regeneration of *p*-bromophenylhydrazine. Attempts to isolate the di-imine in the pure state were, however, unsuccessful. It appears to possess no tendency to form salts or double salts, and does not react with substances such as anhydrous hydrocyanic acid, diphenylketen, etc., at the low temperature necessitated by the unstability of the substance. Tribromophenyl-hydrazine, which might be expected to yield a more stable oxidation product, is unaffected by *p*-benzoquinone. H. W.

Iminoindigotin. ARTHUR BINZ and K. R. LANGE (*Ber.*, 1913, **46**, 1691—1695).—When indigotin is shaken for two hours with alcoholic sodium ethoxide solution and the resultant additive product (compare Binz and Schädel, A., 1912, i, 317) shaken with a solution of zinc hydroxide in ammonia together with an excess of saturated alcoholic solution of ammonia, the resulting blue liquid after acidification with dilute hydrochloric acid deposits *iminoindigotin hydrochloride*; the *sulphate* is also sparingly soluble. The parent substance is evidently more reactive than indigotin, for the blue solution obtained before acidification can be completely oxidised by air to a brown *substance*, whilst hydrogen sulphide reduces the solution to a vat which on re-oxidation yields, not the imine, but a new *substance* which dissolves in alkali to a red, and in alcohol to a brown, solution. The iminoindigo-tin hydrochloride can be reduced by gentle warming with sodium hyposulphite, giving a greyish-white leuco-*compound*. The aqueous solution of the hydrochloride itself dyes wool and mordanted cotton, producing similar shades to indigotin.

If the blue solution obtained by the interaction of the additive compound of sodium ethoxide and indigotin with zinc hydroxide and ammonia is treated with much water instead of with acid, a *zinc* salt, $(C_{16}H_{10}ON_3)_2Zn$, a bluish-green, amorphous substance, soluble in chloroform and acetone, is obtained. This acid character of imino-indigotin is different from the power by which indigotin forms additive compounds because the colour is relatively unaffected.

The free *iminoindigotin*, $C_{16}H_{11}ON_2$ (compare Thiele and Pickard, A., 1898, i, 493), was obtained most satisfactorily by reducing the sulphate with aqueous sodium hydroxide and hyposulphite and re-oxidising the yellow solution; the deep blue product is obtained crystalline with difficulty, and decomposes without melting; it is probably not a pure substance, but possibly a mixture of isomerides, so

that the formula $C_6H_4{<}{\begin{smallmatrix}C(:NH)\\NH\end{smallmatrix}}{>}C{:}C{<}{\begin{smallmatrix}CO\\NH\end{smallmatrix}}{>}C_6H_4$ must be accepted

with reserve. The formation of the substance however, seems to supply further evidence in favour of the view that one-half of the indigotin molecule is more reactive than the second (compare Claasz, A., 1912, i, 513).

The halogen-indigotins, also indigo-red and "thioindigo," likewise form imino-derivatives, whilst by applying methylamine in the original

reaction a methylimino-product can be obtained. These substances also are possibly not homogeneous, and like iminoindigotin, exhibit both acidic and basic tendency.   D. F. T.

Syntheses in the Fatty Aromatic Series. X. Derivatives of Diaryl Paraffins. JULIUS VON BRAUN, H. DEUTSCH, and O. KOSCIELSKI (*Ber.*, 1913, 46, 1511—1526).—Attempts to prepare definite substitution products of diaryl paraffins by sulphonation, chlorination, or nitration have been only partly successful, the compounds obtained showing little tendency to crystallise or to distil without decomposition ; 4 : 4′-dicarboxylic acids have been prepared by the use of oxalyl chloride, but the corresponding amides do not yield any considerable quantity of amines when subjected to Hofmann's reaction. Further attempts to prepare symmetrically substituted dinitro-derivatives have met with slight success, but well characterised tetranitro-derivatives, $C_6H_3(NO_2)_2 \cdot [CH_2]_x \cdot C_6H_3(NO_2)_2$, have been obtained.

A method of obtaining mono-substituted derivatives of diaryl paraffins consists in the condensation of acyl derivatives of chlorinated bases with benzene in the presence of aluminium chloride (compare A., 1912, i, 688), a reaction which is remarkable, since the corresponding nitro-derivatives appear to be unsuitable for the Friedel-Crafts reaction. If, however, the chlorine atom is in the δ- or ε-position with respect to the benzene nucleus, hydrogen chloride is almost entirely eliminated from within the molecule.

4-Benzoylaminodibenzyl, m. p. 170—171°, is obtained in almost theoretical yield by the condensation of *p*-benzoylaminophenylethyl chloride with benzene in the presence of aluminium chloride, and is readily transformed into p-*aminodibenzyl*, colourless leaflets, which are stable to light, m. p. 48°. The latter forms a *hydrochloride*, leaflets, m. p. 210° after darkening at 205°, a *platinichloride*, m. p. 286—289° according to the rate of heating and after darkening from 200°, a *carbamide*,

$$CH_2Ph \cdot CH_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2,$$
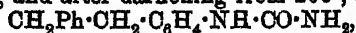
m. p. 155°, and a *phenylthiocarbamide*, m. p. 154°. The constitution of *p*-aminodibenzyl follows from its transformation into dibenzyl by the successive action of nitrous acid and stannous chloride. *4-Iododibenzyl*, m. p. 44—45°, b. p. 210°/10 mm. (slight decomp.), reacts with sodium in much the same manner as does iodobenzene, but more slowly than the latter with copper powder or magnesium. *4-Hydroxydibenzyl* forms yellow leaflets, m. p. 90°, and yields a yellow *sodium* salt with concentrated sodium hydroxide and a *benzoyl* derivative, m. p. 99°. *Dibenzyl-4-carboxylonitrile* is an oil which slowly solidifies when preserved, and is transformed by hydrochloric acid at 120° into *dibenzyl-4-carboxylic acid*, leaflets, m. p. 165°. The azo-dyes obtained from amino- and hydroxydibenzyl closely resemble those obtained from *p*-toluidine and *p*-cresol, so that the authors are led to the conclusion that the number of groups present is of greater importance for the alteration of colour than is the increase in weight of a group already present.

p-Nitrophenylethyl chloride, even after protracted treatment with benzene and aluminium chloride, yields oily products which still contain chlorine, and from which a uniform, chlorine-free nitro-

compound cannot be isolated. *p*-Nitrophenylpropyl chloride behaves in a similar manner.

p-Benzoylaminophenylpropyl chloride condenses with benzene in the presence of aluminium chloride to yield an oily *product*, which, when hydrolysed by hydrochloric acid at 150°, gives a colourless, mobile *base*, b. p. 95—110°/17 mm., which is probably aminohydrindene, $NH_2 \cdot C_6H_3 <^{CH_2}_{CH_2}> CH_2$ (*benzoyl* derivative, m. p. 161°), and p-*amino-diphenylpropane*, b. p. 210—225°/18 mm. (slight decomp.). The latter does not solidify when preserved during several months. It forms a *picrate, benzoyl* and m-*nitrobenzoyl* derivative, all of which are oily. The hydrochloride has m. p. 195°. When heated with methyl iodide (about 4 mols.) and sodium hydroxide, *p*-aminodiphenylpropane yields the corresponding quaternary *iodide*, $Ph \cdot [CH_2]_2 \cdot C_6H_4 \cdot NMe_3I$, colourless needles, m. p. 179—180°, and p-*dimethylaminodiphenylpropane*, b. p. 221—222°/17 mm. The latter is best obtained in the pure state by decomposition of the quaternary iodide in a vacuum. p-*Hydroxy-diphenylpropane* has b. p. 215—220°/18 mm.

o-Aminodiphenylpropane, in contrast to the corresponding *p*-compound, yields a solid m-*nitrobenzoyl* derivative, m. p. 137°. Even with a large excess of methyl iodide it gives solely the tertiary *amine*, b. p. 177—183°/17 mm. (slight decomp.), which, although viscous, does not solidify.

p-*Benzoylaminophenylamyl chloride*, m. p. 210—212°, reacts with benzene and aluminium chloride to yield a *product*, the nitrogen content of which is too high for a normal condensation product (see above).

Only minimal amounts of substance could be obtained by the condensation of acyl derivatives of chloro-bases with thiophen.

The action of oxalyl chloride on a solution of *aζ*-diphenylhexane in carbon disulphide in the presence of aluminium chloride results in the isolation of the *dicarboxylic acid*, $CO_2H \cdot C_6H_4 \cdot [CH_2]_6 \cdot C_6H_4 \cdot CO_2H$, m. p. 303—304°, the *potassium* salt of which is sparingly soluble in water, whilst the *sodium* and *ammonium* salts are more soluble. The corresponding *amide*, m. p. 178°, like the diamide of diphenyloctane-dicarboxylic acid, is converted by bromine and alkali into a dark amorphous mass from which practically nothing can be extracted by acids.

Reduction of the oily product obtained by the nitration of diphenyl-hexane leads to a basic substance, which, when benzoylated, yields a *benzoyl* derivative of indefinite m. p. The latter may be resolved by alcohol into two isomeric portions, the less soluble of which, m. p. 212°, is probably mainly *pp′*-dibenzoylaminodiphenylhexane, and is converted by hydrochloric acid at 140° into a *hydrochloride*, $C_{18}H_{28}N_2Cl_2$, which melts indefinitely at about 205°. The more soluble portion has m. p. 174°.

It is noteworthy, that although the homologues of benzyl chloride readily condense in the presence of sodium with formation of diaryl paraffins, a similar reaction does not occur when the benzene nucleus contains a nitro- or benzoylamino-group.

The preparation of tetranitro-derivatives of diarylparaffins (compare Borsche and Wollemann, this vol., i, 171) is best effected by gradual addition of the hydrocarbon to nitric acid (D 1·52) at −15°. The

mixture is allowed to remain for half an hour in ice and then during two hours at the ordinary temperature, after which it is heated for a few minutes on the water-bath and then poured into water. In this manner diphenylhexane yields $2:4:2':4'$-*tetranitro-aζ-diphenylhexane*, colourless needles, m. p. 90°, which, on oxidation with chromic acid, is converted into 2 : 4-dinitrobenzoic acid. Similarly, *tetranitro-βη-diphenyloctane*, m. p. 145—146°, and *tetranitro-aζ-diphenyl-β : ε-dimethylhexane*, m. p. 112°, are obtained from the corresponding hydrocarbons. Reduction of $2:4:2':4'$-tetranitro-aζ-diphenylhexane in ammoniacal alcoholic solution by means of hydrogen sulphide yields mainly *dinitrodiaminodiphenylhexane*, in which the two amino-groups are probably in the para-position to the hexamethylene chain. (Its *hydrochloride* was also examined.) Smaller quantities of *trinitroaminodiphenylhexane*, m. p. 126—127°, and of an isomeric *dinitrodiaminodiphenylhexane*, m. p. 150—151°, in which the amino-groups are probably in the ortho-position to the hexamethylene chain, are also formed. $2:4:2':4'$-*Tetra-aminodiphenylhexane*, needles, m. p. 138°, is obtained by the reduction of $2:4:2':4'$-tetranitrodiphenylhexane by tin and hydrochloric acid. The *hydrochloride*, m. p. 275°, *picrate*, needles, m. p. 213—215°, *benzoyl* derivative, which is not melted at 280°, and *tetrabenzylidene* derivative, m. p. 151°, were investigated. The base is converted by an excess of boiling acetic anhydride into its *tetra-acetyl* derivative, m. p. 270°; acetylation by glacial acetic acid, in the presence of a few drops of water, gives a *diacetyl* compound, leaflets, m. p. 167°.

Tetra-amino-βη-diphenyloctane,

$$C_6H_3(NH_2)_2 \cdot CHMe \cdot [CH_2]_4 \cdot CHMe \cdot C_6H_3(NH_2)_2,$$
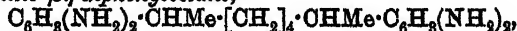
colourless leaflets, m. p. 131°, is obtained in a similar manner from the corresponding tetranitro-compound.   H. W.

Syntheses in the Fatty-Aromatic Series. XI. Double Dye-stuffs from Diarylparaffins. Julius von Braun and O. Koscielski (*Ber.*, 1913, **46**, 1526—1529).—The authors have investigated the effect of the repetition of one and the same chromophore in an organic molecule on the intensity and nature of the colour [compare preceding abstract]. They have prepared double dyes in the azo-, triphenyl-methane-, indamine, and azine series, and do not find any noticeable difference between them and the corresponding mono-dyes.

$2:4:2':4'$-Tetra-amino-aζ-diphenylhexane and tetra-amino-βη-di-phenyloctane when dissolved in dilute acid and treated with sodium nitrite yield reddish-brown colorations exactly similar to that given by 2 : 4-tolylenediamine under similar conditions. On keeping, or immediately in concentrated solution, the "Vesuvines" separate as amorphous, dark brown powders which were not further investigated. When $2:4:2':4'$-tetra-amino-aζ-diphenylhexane is treated with benzenediazonium chloride (2 mols.), the *bis-chrysoidine* separates as a red precipitate. The free *base*,

$$C_6H_{12}[C_6H_2(NH_2)_2 \cdot N_2Ph]_2,$$
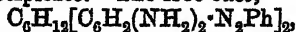
is a yellow, crystalline powder, m. p. 148—150°. The shades given by bis-chrysoidine and by the products derived from tolylenediamine

and tetra-aminodiphenyloctane are scarcely distinguishable from one another.

Tolylenediamine condenses with Michler's hydrol in acetic acid solution to yield the *base*, $CH(C_6H_4 \cdot NMe_2)_2 \cdot C_6H_3Me(NH_2)_2$, m. p. 156—158°. The corresponding *acetyl* derivative has m. p. 200°, and is oxidised by lead peroxide to a product which dyes cotton a pure green. The similar leuco-*base*, obtained from 2 : 4 : 2′ : 4′-tetra-amino-*aζ*-diphenylhexane and Michler's hydrol (2 mols.),

$$C_6H_{12}[C_6H_2(NH_2)_2 \cdot CH(C_6H_3 \cdot NMe_2)_2]_2,$$
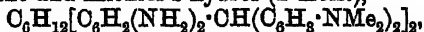
has m. p. 222°. With acetic anhydride it yields a *tetra-acetyl* derivative, m. p. 255—256°, which is oxidised by lead peroxide. The dye so obtained has precisely the same colour as that obtained from tolylenediamine in solutions of similar concentration, and yields precisely the same shades on cotton.

Amorphous *dyes* are obtained by the condensation of 2 : 4 : 2′ : 4′-tetra-amino-*aζ*-diphenylhexane or tetra-aminodiphenyloctane with nitrosodimethylaniline hydrochloride. These give blue colours on the fibres indistinguishable from those obtained with tolylene-blue. When an aqueous solution of these dyes is boiled, the colour changes to red. The "double-reds" so obtained dye the fibres in practically the same shades as tolylene red. H. W.

Amines Derived from Proteins: The Peptamines Glycyl-*p*-hydroxyphenylethylamine, Alanyl-*p*-hydroxyphenylethylamine, and 4-Glycyl-β-aminoethylglyoxaline. MARKUS GUGGENHEIM (*Biochem. Zeitsch.*, 1913, **51**, 369—387).—It is known that by the scission of carbon dioxide from certain amino-acids, such as tyrosine and histidine, bases of pharmacological interest are obtained. The author has consequently undertaken the investigation of similar products from peptides, and with this object has prepared synthetically the substances named above. By the action of chloroacetyl chloride on *p*-hydroxyphenylethylamine, *chloroacetyl-p-hydroxyphenylethylamine*, $C_{10}H_{12}O_2NCl$, m. p. 109°, is obtained, which by the action of aqueous ammonia yields glycyl-*p*-hydroxyphenylethylamine, $C_{10}H_{14}O_2N_2$, m. p. 136°. By the action of bromopropionyl chloride on *p*-hydroxyphenylethylamine, dl-*bromopropionyl-p-hydroxyphenylethylamine*,

$$C_{11}H_{14}O_2NBr,$$

m. p. 98°, was obtained, which yields on treatment with ammonia dl-*alanyl-p-hydroxyphenylethylamine*, $C_{11}H_{16}O_2N_2$, m. p. 116°. By a similar series of reactions, 4-*glycyl-β-aminoethylglyoxaline*,

$$\begin{array}{c} CH{=}N \\ NH \cdot CH \end{array}\!\!\!\!\!>\!\!C \cdot CH_2 \cdot CH_2 \cdot NH \cdot CO \cdot CH_2 \cdot NH_2,$$
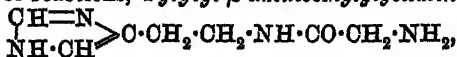
was obtained, the hydrochloride of which melted with decomposition at 250°. The pharmacological action of these substances was investigated and compared with the actions of *p*-hydroxyphenylethylamine and 4-β-aminoethylglyoxaline. The conjugated products have a similar peripheral action on smooth muscle as the simple bases, but the effect is much weaker. The actions were investigated on the uterus, surviving small intestine, the frog's heart, etc., and on the blood-pressures, and the effects are illustrated by numerous tracings. S. B. S.

Purines. X. 6 : 8-Dioxy-2-methylthiolpurine and 8-Amino-6-oxy-2-methylthiolpurine. CARL O. JOHNS and EMIL J. BAUMANN (*J. Biol. Chem.*, 1913, 14, 381—388).—The first orthodiaminoalkyl-thiolpyrimidine has been prepared and condensed to a purine. The presence of the methylthiol group instead of sulphur modified the properties of the new compound, 4 : 5-diamino-6-methylthiol-6-pyrimidone (I). Instead of combining with thiocarbamide to form a thiopurine, as 4 : 5-diamino-2-thio-6-pyrimidone does (this vol., i, 657), it gave an aminopurine (II), which is accounted for by assuming that the thiocarbamide is first transformed into guanidine thiocyanate. The latter substance is, indeed, the best reagent to use for the preparation of the aminopurine, which may even be obtained by employing ammonium thiocyanate. This is remarkable in view of the fact that a similar condensation between other diaminopyrimidines and guanidine salts could not be realised.

$$\underset{\text{(III.)}}{\begin{array}{c} \text{NH}\text{——}\text{CO} \\ \text{C·SMe} \quad \text{C·NH} \\ \text{N}\text{——}\text{C·NH} \end{array}\Big\rangle\text{CO}} \quad \longleftarrow \quad \underset{\text{(I.)}}{\begin{array}{c} \text{NH}\text{——}\text{CO} \\ \text{C·SMe} \quad \text{C·NH}_2 \\ \text{N}\text{——}\text{C·NH}_2 \end{array}} \quad \longrightarrow \quad \underset{\text{(II.)}}{\begin{array}{c} \text{NH}\text{——}\text{CO} \\ \text{C·SMe} \quad \text{C·NH} \\ \text{N}\text{——}\text{C}\text{—}\text{N} \end{array}\Big\rangle\text{C·NH}_2}$$
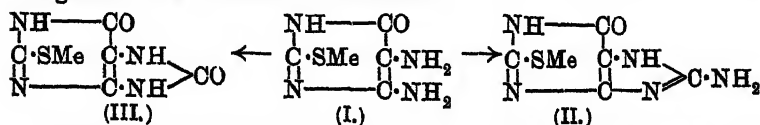
4-Amino-2-methylthiol-6-pyrimidone (A., 1905, i, 836) is best obtained by using methyl sulphate instead of methyl iodide. When it is dissolved in water with sodium nitrite and then acidified with acetic acid, 5-*nitroso-4-amino-2-methylthiol-6-pyrimidone*, $C_5H_6O_2N_4S$, is precipitated as a white solid, which gives a blue solution in acids and a red in alkalis, and decomposes at 255°. It was reduced to 4 : 5-*diamino-2-methylthiol-6-pyrimidone* (I), by means of ammonium sulphide, only just sufficient to discharge the red colour due to the nitroso-compound being added. The substance was dried at 30—40°, and formed colourless crystals, m. p. 211°, which condense with carbamide to form 6 : 8-*dioxy-2-methylthiolpurine* (III) as a granular powder which gives the murexide reaction, is unaltered at 320°, and hydrolyses with difficulty to uric acid. 8-*Amino-6-oxy-2-methylthiolpurine* (II) is also stable at 320°, gives the murexide reaction, and is hydrolysed by acids but not by alkalis, to uric acid.   J. C. W.

Action of Azoimide on Thiocarbimides and Carbimides. Constitution of Azoimide. V. E. OLIVERI-MANDALÀ and F. NOTO (*Gazzetta*, 1913, 43, i, 304—315).—By the action of azoimide on ethylcarbimide the authors have obtained ethylcarbamazide, and from phenylcarbimide, phenylcarbamazoimide, identical with that of Curtius and Hofmann (A., 1896, i, 648). From these results the authors consider it probable that azoimide and the azoimides should have the same structure, and they give reasons for preferring the cyclic formula

$\text{HN}\!\!<\!\!\overset{\text{N}}{\underset{\text{N}}{\|}}$, for azoimide to the chain formula which has been suggested.

By the action of azoimide on phenylthiocarbimide, one of two substances is obtained according to the temperature of reaction; at 40°, one molecule of azoimide reacts, yielding 4-phenyl-3-thiotetrazoline of Freund and Hempel (A., 1895, i, 193), whilst at 60—70° two molecules of azoimide are involved.

Ethylcarbamazoimide, $NHEt \cdot CO \cdot N_3$, prepared in ethereal solution, has b. p. $90°/28$ mm., m. p. 10—$14°$; it forms large, tabular crystals. Its reactions are similar to those of other azoimides containing the group $\cdot NH \cdot CO \cdot N_3$. The action of water yields ethylamine azoimide, whilst alkalis yield ethylamine; the action of aniline on the substance leads to the formation of s-phenylethylcarbamide and aniline azoimide.

The action of azoimide on phenylthiocarbimide in ethereal solution is only complete at 40—$50°$ (under pressure). When the phenylthiotetrazoline produced is dissolved in warm xylene, a decomposition occurs and triphenyli*so*melamine, m. p. $190°$, is obtained. Hofmann (A., 1886, 233) gave m. p. $185°$. Triphenyli*so*melamine platinichloride, $C_{21}H_{18}N_6 \cdot H_2PtCl_6$, was also prepared.

When an ethereal solution of azoimide and phenylthiocarbimide is heated under pressure at 60—$70°$ for twenty-four hours, a *substance*, $C_7H_7N_7S$, is produced, which crystallises in soft, shining scales, m. p. 158—$159°$. When it is boiled with 50% potassium hydroxide, it yields azoimide and the thiocarbimide. Alcoholic sodium hydroxide eliminates 1 molecule of azoimide, yielding thiolphenyltetrazole, m. p. $150°$. In view of these reactions the annexed structural formula is probable for the new substance.   R. V. S.

Supposed Isomerism of Benzeneazoresorcinol. ARTHUR HANTZSCH (*Ber.*, 1913, **46**, 1556—1557).—Two isomeric forms of benzeneazoresorcinol have been described by Will and Pukall (A., 1887, 660). The product, m. p. $161°$, is, in reality, a hydrate containing $\frac{1}{3}H_2O$, which can only be removed with difficulty. The dehydrated product has m. p. 169—$170°$, in agreement with that ($170°$) of the supposed isomeride. A very unstable *monohydrate* is obtained when acetic acid is added to a cooled alkaline solution of benzeneazoresorcinol.   H. W.

[Preparation of Aminoazo-derivatives of Aromatic *m*-Diamines.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 258653).— It is found that $2:4$-diaminophenetole, $2:4$-diaminoanisole, or other ethers of $2:4$-diaminophenols readily undergo bisdiazotisation by the ordinary methods, and when coupled with 2 mols. of a *m*-diamine- (substituted or otherwise) furnish brownish-red *compounds*. $2:4$-*Diaminoanisole* and $2:4$-*diaminophenetole* form colourless needles with m. p. 67—$68°$.

The nitro-ethers can be prepared as described by Willgerodt (A., 1879, ii, 716), and are readily reduced by the ordinary methods.

F. M. G. M.

Nature of the Yellow and Red Helianthine Solutions and Chromoisomerism of Aminoazo-salts. ARTHUR HANTZSCH (*Ber.*, 1913, **46**, 1537—1556).—The solid, red helianthine is dissolved, not only by alkalis, but by all indifferent solvents in the form of yellow helianthine. Red helianthine solutions are only formed in the

presence of hydrogen ions. Yellow helianthine solutions are there-
fore obtained in the absence of hydrogen ions and not merely in the
presence of hydroxyl ions.

Yellow helianthines and red helianthines, as internal sulphonates, are
optically very similar to the yellow and red chromoisomeric salts of
aminoazobenzenes with acids. The generally very unstable, yellow
acid salts are optically quite distinct from the yellow salts of the type
$N_2Ph \cdot C_6H_4 \cdot NMe_2X$, the absorption of which resembles that of azobenzene,
and cannot therefore possess the analogous constitution

$$N_2Ph \cdot C_6H_4 \cdot NMe_2, HX.$$
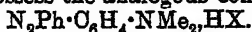
Since the quinonoid character of the red salts, $NHPh \cdot N:C_6H_4:NR_2X$,
is established by the analogy of their absorption with that of
magenta the yellow salts must have the formula

$$C_6H_5 \cdot NHX:N \cdot C_6H_4 \cdot NR_2$$
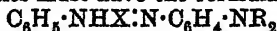
if structural isomerism is assumed. More probably, however, the
yellow salts are themselves quinonoid, since they show a quinonoid
band similar to that of the red salts and the aniline dyes, and hence
must be regarded as valency isomerides of the red salts, thus :
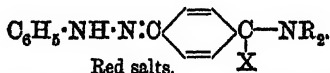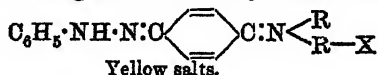
This conception leads to the adoption of a quinonoid structure for
the corresponding aminoazobenzenes, $C_6H_5 \cdot N \cdot N:C_6H_4:NR_2$, since the
latter yield spectra closely analogous to those of the yellow acid
salts.

In a similar manner, the transformation of yellow methyl-orange
into red helianthine probably takes place in the following stages : The
yellow sodium salt present in the alkaline solution is transformed by
neutralisation of the alkali into the corresponding free acid (1) which
immediately passes into the yellow internal salt (2) by wandering of
the hydrogen atom ; this yellow helianthine is converted by acid into
the red valency isomeride (3), which, in the presence of a large excess of
acid, passes into the analogously constituted red hydrochloride (4).
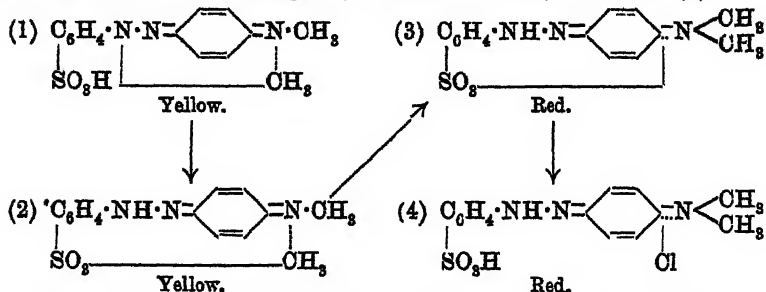
Whilst the dialkylaminobenzenes, including the halogenalkylates,
which are incapable of isomerisation yield three series of salts, the

simple aminoazobenzenes can yield also a fourth graphite-black series which are possibly constituted according to the formula

$$C_6H_5 \cdot NH(HX) \colon N \colon C_6H_4 \cdot NH.$$
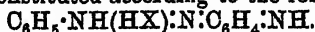
Red helianthines are best obtained in the pure condition by means of their *pyridine* salts, which, when dried at $100°$, lose pyridine, leaving the pure helianthine.

Ethyl dimethylanilineazobenzoate, $NMe_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot CO_2Et$, forms leaflets of a reddish-golden colour, m. p. $160°$. H. W.

[Preparation of Compounds Containing 3 : 4-Dihydro-1 : 4-oxazine-3-one Ring.] AKTIEN-GESELLSCHAFT FUR ANILIN-FABRIKATION (D.R.-P. 259700).—When the azo-compounds obtained from 1-amino-2-naphthoxyacetic acids or 2-aminophenoxyacetic acids which contain an alkyl or alkyloxy-group in the meta-position are treated with acids, they lose water and furnish cyclic compounds according to the following scheme; and dyes in which X is represented by benzidine and other amino-compounds are described in the original. F. M. G. M.
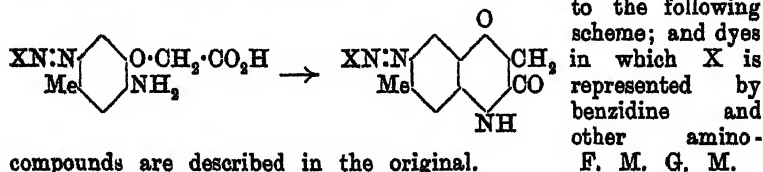
Amount of *l*-Tyrosine in Proteins and the Accuracy of the Estimation of this Amino-acid. EMIL ABDERHALDEN (*Zeitsch. Physiol. Chem.*, 1913, 85, 91. Compare this vol., i, 409).—*l*-Hydroxyproline, like tyrosine, shows a blue coloration with the Folin-Denis reagent. The preparation used had $[\alpha]_D^{20} -72.37°$. A synthetic product made by Leuchs has $[\alpha]_D^{20} -76°$, whereas the value usually given is $[\alpha]_D^{20} -81°$. Since tryptophan and hydroxytryptophan also react with the Folin-Denis reagent, their method for estimating tyrosine is of no value. E. F. A.

The Oxidative Degradation of the Proteins. OTTO EISLER (*Biochem. Zeitsch.*, 1913, 51, 26—44).—On oxidation of proteins with calcium permanganate, "peroxyprotic" acids are produced, which, according to von Furth, undergo hydrolysis with barium hydroxide with scission of oxalic acid, yielding deaminoprotic acids, which on further oxidation with permanganate yield "kyroprotic" acids. These, on treatment with barium hydroxide yield deaminokyroprotic acids. The deaminokyroprotic acid from caseinogen was prepared and described. The mercury salt contained 18.35% C, 2.62% H, 5.04% N, 0.4% S, 59.3% Hg, 1.7% amino-acid nitrogen (estimated by van Slyke's method), and 0.44% basic nitrogen. The probable constitution of this acid is discussed by the author. Sericoin was also prepared from silk-waste by Weyl's method. This also was submitted to oxidation by calcium permanganate, and the product hydrolysed by barium hydroxide. The substance thus obtained could not be oxidised further by permanganate in the cold. The mercury salt contained 8.02% C, 1.06% H, 3.40% N, 12.85% O, and 74.67% Hg. The amino-acid nitrogen was 2.21%, and the basic nitrogen 1.72%. The high

percentages of the latter and of the mercury are remarkable. They indicate that the simpler amino-acid groups are removed by oxidation, leaving the more basic groups intact, which seems to show that the protein is built up by branched chains from a more stable residue of diamino-acids.   S. B. S.

The Amounts of Indole Produced by the Artificial Digestion or Putrefaction of Various Proteins. WACLAW VON MORACZEWSKI (*Biochem. Zeitsch.*, 1913, **51**, 340—354).—The amount of indole obtainable from various proteins by successive digestion with pepsin, trypsin, and putrefactive bacteria, both under the simplest conditions and in the presence of various foreign substances, such as fats, sugars, bile, etc., was estimated. The results are tabulated.   S. B. S.

Hæmoglobin. The Magnesium Derivative of Mesoporphyrin. JEAN ZALESKI (*Ber.*, 1913, **46**, 1687—1691).—In order to introduce magnesium into mesoporphyrin (compare Willstätter and Forsén, this vol., i, 499), the substance is treated with magnesium, methyl or ethyl iodide, and a trace of iodine in ethereal solution ; the product is a *compound*, $C_{38}H_{46}O_8N_4Mg$, or $C_{39}H_{48}O_8N_4Mg$, m. p. 335°, which in its absorption bands and easy scission of magnesium on treatment with dilute acid closely resembles rhodophyllin (Willstätter, A., 1908, i, 198) ; the *substance*, m. p. near 288°, obtained by elimination of magnesium, is distinct from the ethyl ester of mesoporphyrin originally taken.   D. F. T.

Methæmoglobin. BÉLA VON REINBOLD (*Zeitsch. physiol. Chem.*, 1913, **85**, 250—285).—It is regarded as established that methæmoglobin takes a middle position between hydroxyhæmoglobin, $Hb{<}^O_{()}$, and reduced hæmoglobin, Hb. It is uncertain whether it has Zeynek's formula $Hb(OH)_2$ or Küster's formula Hb–OH.

It is now proved by spectrophotometric and gasometric measurements that the reaction between potassium ferricyanide and hydroxyhæmoglobin is quantitative, one molecule of the cyanide being required to displace a molecule of oxygen as shown by the equation

$$Hb{<}^O_O + K_3FeCy_6 + H_2O = Hb·OH + K_4HFeCy_6 + O_2,$$
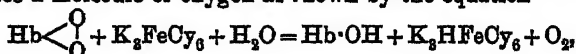
which is in agreement with Küster's formula.   E. F. A.

Keratin of White Human Hair. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, **85**, 246—249).—The result of hydrolysing white human hair is as follows : Glycine, 9·12 ; alanine, 6·88 ; leucine, 12·12 ; glutamic acid, 8·0 ; phenylalanine, 0·62 ; tyrosine, 3·3, and cystine, 11·55%. The amounts of cystine, glycine, and alanine are abnormally large. Hair keratin closely resembles that from sheep's wool.
        E. F. A.

Keratin of the Scales of Manis japonica. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, **85**, 241—245).—The keratin of *Manis japonica* yields amino-acids on hydrolysis, namely, glycine 1·33%,

alanine 120%, valine 4%, leucine 10 25%, 'proline 3·5%, glutamic acid, 3·5%, phenylalanine 2·67%, tyrosine 13%, and cystine 4·5%. The amount of alanine is abnormal, other keratins yielding 1·2%—1·8%. The proportion of tyrosine is likewise unusually large.   E. F. A.

Keratin of Snake Skins (Boa Constrictor and Python). HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, **85**, 335—340).—The distribution of the nitrogen and the percentage of certain monoamino-acids is determined in the keratin of snake skins, and compared with that in other keratins. The distribution of the nitrogen is much the same in all keratins, but they differ widely in the proportions of the individual amino-acids which they contain. Snake-skin keratin contains a high proportion of tyrosine and leucine.   E. F. A.

Action of Quinones on Wool and Other Protein Substances. WILHELM FAHRION (*Zeitsch. angew. Chem.*, 1913, **26**, 328. Compare *ibid.*, 1909, **22**, 2138).—A claim for priority against Scharvin (this vol., i, 661).   H. W.

Reactions on Dyeing Animal Fibres. WILHELM SUIDA (*Zeitsch. physiol. Chem.*, 1913, **85**, 308—323).—Wool loses more of its substance in a faintly acid bath than in a neutral bath when heated under the conditions usual for dyeing. The difference is especially marked on subsequent treatment with an alkaline bath. Wool in both cases mainly gives up basic substances to the bath, so that, normally, during dyeing the wool itself becomes acid.

When wool is heated with phenols and acetic acid, the presence of the phenol on the fabric cannot be established, using ferric chloride. The substituted nitrophenols dye the wool, the intensity increasing with the acidity of the phenol. These colours are readily removed by faintly alkaline washes.

Wool fixes phenolcarboxylic acids, but no ferric chloride reaction is shown, indicating that the phenylhydroxyl group has combined with some constituent of the wool.

Whereas *p*-benzoquinone, toluquinone, *o*-3 : 6-xyloquinone, etc., in a weak acetic acid bath dye wool intensely, *p*-2 : 5- and *m*-2 : 5-xyloquinone, also thymoquinone, anthraquinone, and phenanthraquinone have no such action. The active para-quinones all contain the grouping –CO·CH:CH·CO–, which is absent from the inactive quinones.

Naphthazarin, a dihydroxy-α-naphthaquinone, dyes wool a deep violet-brown. The colour is not removed even by strong ammonia.

The quinones are supposed to give rise to quinoneanilide-like compounds with the amino-substances of the wool. Silk is not dyed so quickly by quinones as wool.   E. F. A.

Precipitation of Enzymes from their Solutions by Moist Aluminium Hydroxide. WILLIAM H. WELKER and JOHN MARSHALL (*J. Amer. Chem. Soc.*, 1913, **35**, 822).—When solutions of the following enzymes were shaken with moist aluminium hydroxide, the enzymes were quantitatively removed: peroxydase and oxydase (aqueous extract of potato), pepsin (aqueous or 0·2% HCl solution), rennin

(aqueous solution), trypsin (0·5% Na_2CO_3 solution, 30% alcoholic extract of pancreas, or 30% alcoholic extract of pancreas containing an equal volume of 1% Na_3CO_3), and amylase and lipase (30% alcoholic extract of pancreas). The amylase of saliva was not completely removed by this treatment; the filtrate was capable of converting starch paste into soluble starch, but could not effect further hydrolysis. Pepsinogen could be precipitated quantitatively, but only with great difficulty.   E. G.

Action of Hydrogen Chloride and Ammonia Gas on Invertase. VI. THEODOR PANZER (*Zeitsch.physiol. Chem.*, 1913, 85, 225—230. Compare this vol., i, 113, 541, 662).—Invertase, when treated in turn with dry hydrogen chloride and dry ammonia, does not recover its hydrolytic activity. The groups destroyed by the acid are not restored when this is neutralised as is the case with diastase. This behaviour is regarded as further evidence in favour of the formation of anhydride by the action of the acid.   E. F. A.

Action of Nitrous Oxide on Invertase. VIII. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, 85, 392—398).—On subjecting invertase to the action of dry nitrous oxide, oxidation takes place, and subsequently a little nitrous oxide is fixed by the enzyme. The hydrolytic activity of the enzyme is not affected. The treatment increases the acidity of the enzyme, although in one instance the acidity decreased. The amount of amide and amino-nitrogen is less after treatment. The experiments again emphasise the difference between invertase and diastase.   E. F. A.

Action of Hydrogen Chloride and Ammonia on Diastase. V. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, 85, 97—111).—The action of dry hydrogen chloride and ammonia separately on diastase has already been studied (compare this vol., i, 113, 541). The enzyme has now been treated first with hydrogen chloride, and then with an excess of dry ammonia gas. The resulting increase in weight, acidity and nitrogen, shown by means of formaldehyde, was the same as when the enzyme was acted on by ammonia alone. The treatment with ammonia restores the hydrolytic activity of the diastase, whereas if the enzyme, after treatment with hydrogen chloride, is neutralised with aqueous ammonia, it remains inactive.
                                                         E. F. A.

Action of Nitrous Oxide on Diastase. VII. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, 85, 292—307).—Dry nitrous oxide gas was passed over diastase in the manner described for hydrogen chloride or ammonia. Whereas an enzyme preparation containing milk sugar absorbed about 3% of the gas, a purified enzyme material absorbed three times this amount. Only a small quantity of the gas can be pumped off in a vacuum. The nitrous oxide does not cause either hydrolytic decomposition or anhydride formation. The hydrolytic activity of the purified enzyme is largely destroyed by the treatment, but the presence of the milk sugar protects the enzyme from harm.
                                                         E. F. A.

Action of Salts of Metals on the Saccharification of Starch by Amylolytic Ferments. C. GERBER (*Bied. Zentr.*, 1913, **42**, 265—268; from *Compt. Rend. Soc. Biol. Paris*, 1911, **70**, 139, 391, 547, 724, 726, 728).—Alkali salts of monobasic acids increase the rate of saccharification when present in small amounts, whilst large amounts have a retarding effect; acid salts act similarly to the corresponding acids. The salts of monobasic organic acids act similarly; the retarding effect increases with the mol. wt.

Magnesium salts in small amounts have no action, and larger amounts have a retarding effect. Manganese, ferric and aluminium salts have a quickening effect in small amounts, and a retarding effect when present in large quantities. Ferrous salts retard or inhibit saccharification according to the amount.

Cadmium and zinc in very small amounts have a retarding effect, whilst moderate amounts inhibit saccharification. Still larger amounts, up to a certain point, are, however, favourable. Similar results were obtained with copper and gold salts.

Salts of platinum and palladium in very small amounts are favourable; the action is very suddenly reversed as the amounts increase.　　　　　　　　　　　　　　　　　　　　　　　　　N. H. J. M.

Synthesis of Glucosides of the Alcohols by means of Emulsin; Reversibility of Ferment Actions. ÉMILE BOURQUELOT and MARC BRIDEL (*Ann. Chim. Phys.*, 1913, [viii], **28**, 145—218).— A résumé and discussion of results already recorded in the following abstracts: 1906, ii, 386; 1911, i, 1053; 1912, i, 522, 592, 593, 672, 738, 790, 928, 946; this vol., i, 212, 303.　　　　　　　　　　　T. A. H.

Behaviour of Emulsin in Presence of Pyridine. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, **85**, 415—426).—β-Glucosides are hydrolysed by emulsin in presence of 12% of pyridine. When the proportion of pyridine is increased, hydrolysis is retarded, and ceases in 20% solution. In presence of pyridine, amygdalin is converted into *iso*amygdalin.　　　　　　　　　　　　　　　　　　　　　　　　　E. F. A.

Use of Increasing Proportions of Dextrose in the Bio-chemical Synthesis of β-Methylglucoside. Influence of the Glucoside Formed on the Arrest of the Reaction. ÉMILE BOURQUELOT and ÉM. VERDON. (*Compt. rend.*, 1913, **156**, 1638—1640; *J. Pharm. Chim.*, 1913, [vii], **7**, 575—579).—In methyl alcohol (70%) the quantity of glucoside formed increases proportionately as the quantity of dextrose in solution increases up to 12%, above which the amount of glucoside formed diminishes slightly. The presence of methylglucoside in the solution has a marked inhibiting effect on the amount of glucoside synthesised. The quantity of glucoside necessary to check the reaction is proportional to the amount of dextrose in the solution.　　　　　　　　　　　　　　　　　　　　　　　　　W. G.

Enzyme Action. XIX. Urease. II. Observations on Accelerative and Inhibitive Agents. HENRY E. ARMSTRONG, M. S. BENJAMIN, and EDWARD HORTON (*Proc. Roy. Soc.*, 1913, *B*, **86**, 328—343. Compare A., 1912, i, 594).—The manner in which the

activity of urease is affected by the presence of various substances together with the urea has been studied throughout the whole course of the change with considerable accuracy. The results are expressed graphically.

Both strong acids and carboxylic acids such as $M/50$ aspartic and salicylic acids prevent action. Boric acid in all strength retards action. Guaiacol and resorcinol at first retard and subsequently accelerate hydrolysis. p-Benzoquinone is poisonous, and quinol and quinol monomethyl ether, both of which are easily oxidised to p-benzoquinone, soon stop action. Glycine, asparagine, and carbonic acid all accelerate action.

It is emphasised that in presence of carbonic acid the rate of change approximates to a "linear" character.

Hydrogen cyanide accelerates action.

Saligenin, acetaldehyde, benzaldehyde and salicylaldehyde are moderately active depressants.

It is considered that enzymic changes would be found to take place at approximately constant rates were it not that they are subject directly and indirectly to considerable retardation by the products of change; probably the products of change have an affinity for the enzyme which is actually greater than that which obtains between the hydrolyte and the enzyme.

Enzyme action takes place entirely at the surfaces of colloid particles suspended in the solution of the hydrolyte, and not between substances which are all in true solution.   E. F. A.

Fermentations with Yeast in the Absence of Sugar. XI. Carboxylase. CARL NEUBERG and P. ROSENTHAL (*Biochem. Zeitsch.*, 1913, 51, 128—142).—The carboxylase from yeast, which causes the decomposition of pyruvic acid, can be distinguished from the sugar ferment (zymase) by various reactions. The latter does not act in the presence of chloroform, whilst the former retains its full activity, especially in the presence of "buffers," which prevent great changes in the reaction of the fermenting liquid. For this latter purpose, solutions of either alkali salts of pyruvic acid in the presence of free arsenious or boric acids or free pyruvic acid in the presence of borates or arsenites can be used. Similar results were obtained both with fresh and dried yeasts of pure culture. The carboxylase acts in a much shorter time than the zymase. Furthermore, if maceration juices are preserved at room temperature, the zymase activity is readily lost, whereas the carboxylase remains active over comparatively long periods. Furthermore, the zymase is readily destroyed by heating to 50°, whereas the carboxylase activity remains intact. There is a further difference in that the zymase loses its activity on dialysis, whereas the carboxylase does not, especially if the dialysed solution is kept for some time. Attention is called to the fact that the fermentation of sugar must precede in stages, the C_6-sugar being apparently broken down into C_3-substances, such as pyruvic acid. The ferment causing the evolution of carbon dioxide from the latter can remain intact, even after the zymase is destroyed.   S. B. S.

Paralysis and Activation of Zymase and Catalase. HENRI VAN LAER (*Centr. Bakt. Par.*, 1913, ii, **37**, 529—534. Compare A., 1912, i, 1043).—In an earlier paper it was stated that the addition of papain depresses, and malt extract increases, the activity of zymase and catalase. The former is attributed to impurities in the juice of the *Carica papaya* which digest the two enzymes.

The activation of the enzymes by extract of malt may be due, firstly, to direct stimulation of the zymase and catalase by impurities in the extract of malt; secondly, by inhibition of the antagonistic enzyme (protease) by impurities, or else to the existence of pro-enzymes—prozymase and procatalase—combinations of the enzymes with a carbohydrate, such compounds being saccharifiable by amylase.

Experiments with a Munich bottom yeast and a Mons top yeast have been made, and again show a depressing action of the papain on the catalase and zymase in the yeast juice. Tests with extract of malt exhibit activation of the enzymes during the initial stages of the experiment with a pronounced depres-ion later on. This action is ascribed to the presence of proenzymes in the yeast-juice. At the moment of fission a positive effect is produced, and this is followed by their digestion by impurities in the malt extract.   H. B. H.

Arseno-compounds. AUGUST MICHAELIS and ARTHUR SCHÄFER (*Ber.*, 1913, **46**, 1742—1743).—Since arsenic compounds frequently have a higher molecular weight than the corresponding nitrogen compounds, the authors have determined the molecular weight of arsenobenzene and *p*-arsenotoluene respectively.

Arsenobenzene, slender, white needles, has m. p. 212°, not 196° as previously given (A., 1881, 722). It is readily oxidised in solution to phenylarsine oxide, which, even in small quantities, greatly depresses the m. p. A solution of arsenobenzene in benzene, when allowed to evaporate spontaneously in contact with air, leaves a resinous product consisting solely of phenylarsine oxide. In boiling benzene solution, arsenobenzene has mol. wt. at 399·8 (calc. 304).

p-Arsenotoluene separates from benzene in small plates, m. p. 202° (from chloroform, however, in needles, m. p. 184°; compare A., 1902, i, 411). In solution, it is readily oxidised to *p*-tolylarsine oxide. It has a normal molecular weight when dissolved in dry phenol. In the presence of a trace of moisture, on the other hand, a constant freezing point of the solution is not observed.   H. W.

The Displacement of Metals from their Phenyl Compounds. SIEGFRIED HILPERT and GERHARD GRUTTNER (*Ber.*, 1913, **46**, 1675—1691).—Although the action of various metals on the organo-metallic compounds has been fairly well investigated in the aliphatic series, the corresponding behaviour with the compounds of the phenyl series has been less well studied (compare Hilpert and Grüttner, A., 1912, i, 939). It is now discovered that at the temperature of the experiment (200—350°) the metals of comparatively low m. p. generally react with the organo-metallic compounds causing a displacement of the other metal, and that it the two metals do not affect one

another the reaction may proceed quantitatively. If the m. p. of the resulting mixture of metals lies below the temperature of the experiment the extent of the interaction appears to be dependant on the relative quantities of the two metals in the mixture.

Magnesium and aluminium react with mercury diphenyl so readily that no external heating is necessary; magnesium diphenyl (compare Fleck, A., 1893, i, 622) does not inflame in the air unless breathed upon; it forms feathery needles (from ether), which melt at the temperature of the hand, almost immediately afterwards passing into the ether-free, amorphous substance. For the reaction between zinc and mercury diphenyl (in a hydrogen atmosphere), heat has to be applied when the chemical change occurs with quantitative displacement of mercury; zinc diphenyl, needles, m. p. 105—106°, b. p. 280—285°, both in hydrogen, is very sensitive to air and moisture, the former converting it into zinc oxide and diphenyl, and the latter into zinc hydroxide and benzene; it is inflamed by fuming nitric acid, and reacts with chloroform, producing triphenylmethane; with iodine in benzene solution it produces zinc phenyl iodide, which is slowly converted further into zinc iodide; with mercury it reacts to a small extent, giving a trace of mercury diphenyl.

Contrary to expectation, aluminium reacts scarcely at all with zinc diphenyl, possibly on account of the protecting film of oxide; in order to determine the relative reactivity of these two metals towards the metallic phenyl compounds, the two metals were allowed to react simultaneously with the same quantity of mercury diphenyl under such conditions that the zinc if alone would form zinc diphenyl; it was found that the relative amounts of aluminium triphenyl and zinc diphenyl were 99 : 1. Magnesium decomposes completely the phenyl derivatives of aluminium and zinc, whilst mercury has no effect on them; the metals magnesium, aluminium, zinc, and mercury, therefore, stand in the same relative order of activity as in the ordinary potential series.

Cadmium exhibits but little tendency to form organo-metallic compounds and with the mercury alkyls gives rise only to hydrocarbons; with mercury diphenyl it is found that cadmium reacts, forming cadmium diphenyl, but the extent of the reaction depends on the composition of the liquid cadmium amalgam produced, and therefore on the relative amount of cadmium applied; by using an apparatus in which the liquid reaction product could be repeatedly treated in a hydrogen atmosphere with fresh cadmium until more than ten atomic proportions had been applied, a specimen of *cadmium diphenyl*, colourless prisms containing 25% of mercury diphenyl, was obtained; it is stable when dry, but in benzene solution it undergoes atmospheric oxidation. From the amount of cadmium necessary in the above experiment and the fact that the product when heated with excess of mercury quantitatively regenerates mercury diphenyl, it is evident that cadmium falls after mercury in the series, showing the relative activity of the metals towards the formation of phenyl compounds.

The behaviour of bismuth is somewhat analogous to that of cadmium; mercury diphenyl heated with an excess of bismuth and bismuth triphenyl heated with an excess of mercury both yield a mixture of

the phenyl derivatives of the two metals ; the relative proportions in the mixed products indicate that bismuth falls before mercury in the series indicating relative activity in these compounds. With the six metals investigated above, therefore, cadmium alone falls into a position different from that occupied in the ordinary potential series.

The quadrivalent metals lead and tin appear to form a special class, for they fail to react with mercury diphenyl, whilst their tetraphenyl derivatives are entirely unaffected by magnesium.

The behaviour of the metallic haloids towards metallic phenyl compounds is very different from that of the corresponding free metal. Mercuric bromide reacts quantitatively with an ethereal solution of magnesium phenyl bromide producing *mercury phenyl bromide*, leaflets, m. p. 275°, if the original reagents are in approximately equimolecular proportions; with an excess of the organo-magnesium compound, mercury diphenyl is formed, but in only 40% yield. In a similar manner, mercury a-naphthyl bromide, m. p. 203°, can be produced, which even with a large excess of magnesium a-naphthyl bromide gives only a small quantity of the diphenyl compound. Cadmium chloride also reacts with magnesium phenyl bromide and magnesium a-naphthyl bromide, but the products were not isolated.

It is remarked that the sensitiveness of the phenyl compounds towards air and water diminishes with increasing atomic weight and electro-negative character of the metal.

The action of the alkali metals on mercury diphenyl or zinc diphenyl, with or without a solvent, was never found to yield a deposit of mercury until water was added (compare Acree, A., 1903, i, 724), and it is believed that an additive product is first produced.

In agreement with the earlier negative results (Smith, Barnett and Hall, A., 1900, i, 89) on the existence of a tungsten methyl iodide (Cahours, 1862), the authors were unable to isolate any compound of such nature. D. F. T.

Physiological Chemistry

Narcosis. I. The Relationship between Narcosis and Oxygen Respiration. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1913, **51**, 143—170).—The author gives a critical review of the various experiments which indicate a relationship between narcosis and diminution of oxygen respiration. He draws the conclusion that narcosis cannot be explained simply as a result of diminished oxidation, citing amongst other experiments the fact that certain ascarids, which are anoxybiotic, are particularly susceptible to narcosis. It seems more probable that narcosis and inhibition of oxidation are concomitant results of some more general action.

S. B. S.

The Chlorine Content of Blood and its Division between the Corpuscles and Serum. The Permeability of Corpuscles for Inorganic Substances. J. SNAPPER (*Biochem Zeitsch.*, 1911, 51, 53—61).—The chlorine was estimated in the total blood, and in the serum and corpuscles separately. It was found that the ratio of the chlorine in the corpuscles to that in the serum was approximately constant both in the dog and in man, being about 40%. As this is very nearly the ratio of the intraglobular fluid to the total volume of the erythrocytes as found by Hamburger, the conclusion is drawn that there is an even distribution of the inorganic contents of blood between the serum and the formed elements.   S. B. S.

Formation of Methæmoglobin. WOLFGANG HEUBNER (*Arch. expt. Path. Pharm.*, 1913, 72, 241—281).—Whereas the injection of phenacetin into the blood of carnivora causes the formation of methæmoglobin, dimethylphenacetin is without effect. Phenacetin outside the body has no action on blood, indicating that the active substance is formed from it in the organism.

Parallel experiments with derivatives of o-, m-, and p-aminophenols show the meta-derivatives to be barely poisonous, and, whereas the ortho- and para-derivatives are equally poisonous for dogs, the ortho-compound is the stronger in the case of cats, which are extremely sensitive to both aminophenols. Rabbits are resistant to these poisons.

Since each aminophenol molecule reacts several times with hæmoglobin molecules, the reaction is explained on the hypothesis that the o- and p-aminophenols are oxidised to o- or p-benzoquinone-imine, and that this actually reacts with hæmoglobin, $2(Hb\dot{:}Fe)$, forming aminophenol and methæmoglobin, $2(Hb\dot{:}Fe\cdot OH)$. The change involves conversion of bivalent into tervalent iron, the active agent being the quinone. This is in agreement with the formation of hæmoglobin by the agency both of oxidising and reducing agents.

Quinol acts similarly, but has no effect in the absence of oxygen. p-Benzoquinone works energetically in the absence of oxygen.

Quinol and catechol readily produce methæmoglobin in test-tube experiments, whereas resorcinol is without effect. Similarly, pyrogallol is active, chloroglucinol inactive.

Aniline is active, dimethylaniline has no effect, although the isomeric m-xylidine is also active in producing methæmoglobin.

The substitution of the para- and of both ortho-positions in aniline by chlorine does not alter its activity. Apparently the aniline nitrogen is oxidisable without oxidation previously taking place at the ortho- or para-positions in the nucleus to form a quinone. Acetylation of the nitrogen in trichloroaniline has little effect; in dichloroaniline some lessening of the activity is brought about on acetylating.

Hæmoglobin is oxidised by hydroxylamine even in the absence of oxygen. The introduction into aniline derivatives of two methyl groups occupying the one the ortho-position to nitrogen, and the other either the ortho- or para-position lowers the oxidising

activity. Phenetidine, for example, has hardly any action in producing methæmoglobin.

Emphasis is laid on the difference between rabbits, dogs, and cats in the reactions between the blood and aromatic oxidising agents.

The spectrum of pure methæmoglobin does not show the two oxyhæmoglobin bands in the yellow and green. When these are seen, oxyhæmoglobin is present as impurity. E F. A.

The Change in the Permeability of Blood Corpuscles on Addition of Acid. J. SNAPPER (*Biochem. Zeitsch.*, 1913, 51, 62—88).—The results of Hamburger are confirmed, according to which the addition of acid causes a swelling of the corpuscles and a passage of chlorine from the serum into the corpuscles. The influence of the addition of acids to the blood both *in vivo* and *in vitro* was investigated. The diffusible and non-diffusible alkali was estimated. For this purpose, the total serum was titrated with $N/25$-tartaric acid, and also the filtrate after precipitation with alcohol, which throws down the proteins with the alkali combined with proteins (non-diffusible alkali). Congo-red paper was used as indicator. Both *in vivo* and *in vitro*, there was found to be a relative increase of the diffusible as compared with the non-diffusible alkali as a result of the action of acids. A possible explanation of the action of acids as regards the distribution of chlorine between serum and corpuscles seemed therefore to be the relative increase of ·SO_4 ions in the corpuscles when sulphuric acid was employed, as compared with the serum, due to the larger amount of alkali set free from proteins in a diffusible form and a subsequent interchange of ·SO_4 and Cl ions between serum and corpuscles. As, however, a change in distribution of chlorine could not be brought about by addition of neutral sulphates alone without addition of acids, this explanation is inadequate. It is assumed, therefore, that the acids act on the proteins and so alter the permeability of the cells to ions. A similar change of distribution could not be brought about by lipoid solvents, such as chloroform, even when the latter is present in sufficient quantities to cause a small amount of hæmolysis. S. B. S.

The Biological Significance and Metabolism of the Proteins. VII. The Amino-Nitrogen Titratable in the Presence of Formalin in the Blood Corpuscles of Various Animals. A. COSTANTINO (*Biochem. Zeitsch.*, 1913, 51, 91—96).— The proteins were separated by barium salts by the method of Buglia and Costantino. In both the serum and corpuscles, nitrogenous substances titratable in the presence of formalin were found. The quantity found was small in the case of serum, but relatively large in that of corpuscles. In non-nucleated, the quantity is only about half that existing in nucleated corpuscles. In the case of mammals and turkey, the amount found in the serum is about the same. The author calls attention to the importance of examining chemically the corpuscles when investigating various problems of metabolism. S. B. S.

Hæmolysis by Chemical Agents. PHILIPP EISENBERG (*Centr. Bakt. Par.*, 1913, **1**, 69, 173—225).—The author has carried out a long series of experiments on the action of salts, acids, alkalis, and various organic substances (including tetanolysin and vibriolysin) on blood corpuscles. He has investigated, amongst other factors, the influence of hypertonicity, synergism, and antagonism. He summarises his results, from which, however, no extensive generalisations can be made.   S. B. S.

Blood Lipoids and Phagocytosis. B. STUBER (*Biochem. Zeitsch.*, 1913, **51**, 211—233).—A method is described by means of which the phagocytic index of leucocytes can be determined, thrush spores being employed as the foreign object, as they can be readily stained by Leishmann's method. For *in vitro* experiments human blood was employed, and for *in vivo* experiments cats and sometimes rabbits were used. It was found that cholesterol by itself greatly diminishes the phagocytic index, whereas lecithin has no action. On the other hand, lecithin greatly diminishes, and even obliterates when in sufficient quantity, the power of cholesterol to reduce the phagocytic index, provided that it has not been previously heated. If the cholesterol and lecithin are heated after mixing, they do not together diminish the phagocytic index. Similar results were obtained by both the *in vivo* and *in vitro* experiments. It appears, therefore, that cholesterol acts directly on the phagocytes, and destroys their phagocytic action, but in the presence of lecithin a lecithin-cholesterol compound is formed. This cannot, however, be produced if lecithin is heated before the two substances are mixed.   S. B. S.

The Acetonitrile Reaction. FR. PORT (*Biochem. Zeitsch.*, 1913, **51**, 224—228. Compare Reid Hunt, A., 1905, ii, 847; 1910, ii, 736; Trendelenburg, A., 1911, ii, 50).—The author throws doubt on Reid Hunt's acetonitrile reaction with mice for detection of thyreogenic substances in the blood on the ground that the susceptibility of the animals to the poison is so very variable that it is impossible to determine the limiting dose.   S. B. S.

Influence of Fatigue on the Amount of Dialysable Compounds, which React with Triketohydrindenhydrate, in the Serum. EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, **85**, 136—142).—After severe fatigue in the dog, the blood-serum contains less of the substances referred to in the title. Admixture of the serum either of normal or fatigued dogs with cooked muscle produced no change. A similar result was obtained with other tissues.   W. D. H.

The Fermentative Properties of Blood. I. A Peptolytic Ferment of Normal Dog's Serum. LUDWIG PINCUSSOHN (*Biochem. Zeitsch.*, 1913, **51**, 107—115).—It is known that by injection of various proteins into animals, the blood acquires peptolytic properties. The author shows that normal dog's serum

possesses a ferment capable of hydrolysing the peptone of dog's muscle, prepared by treating the muscular tissue with 70% sulphuric acid in the cold, and precipitating by alcohol, after the removal of the sulphuric acid with barium hydroxide. The serum does not, however, digest a similar peptone prepared in the same way from cat's muscle, or other peptones from foreign substances.

S. B. S.

The Influence of Diet on the Activity of Ptyalin. H. VAN TRIGT (*Zeitsch. physiol. Chem.*, 1913, **85**, 156—160).—The author examined his saliva at frequent intervals; each meal increased its diastatic activity; the increased action was greatest after a carbohydrate meal, and least after a protein meal. W. D. H.

Fluorine in the Animal Organism. II. Skeleton, Cartilages, and Tendons. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1913, **156**, 1425—1430. Compare this vol., i, 677).—An examination of bones, teeth, cartilage, and tendons for fluorine. Bones and teeth, either human or animal, are comparatively rich in fluorine, the content of the diaphyse portion of the bones being about four times as great as that of the epiphyse, in the case both of an elderly man and a new-born infant. The teeth approach the diaphyse in fluorine content. The skeleton of fish contains practically the same amount of fluorine as the scales, and a complete analysis of these organs shows a marked analogy. Cartilage and tendons are very low in fluorine content. W. G.

Is it Possible Artificially to Increase the Amount of Phosphatides in Brain? ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1913, **51**, 407—422).—Commercial preparations of kephalin, when administered by the mouth, are well tolerated, and all but a small percentage is resorbed. Its ingestion causes an increased phosphoric acid output in the urine, both absolute and relative as compared with the nitrogen. In contrast to egg-yolk lecithin, kephalin does not accumulate in the liver, but appears to accumulate in the brain. Rabbits were used for the experiments, and the quantities of phosphatides in the organs were estimated by the following method. The organ (brain) was first extracted with hot alcohol, and the residue was then extracted with a mixture of equal volumes of absolute alcohol and benzene. The residues from both extracts were then dissolved in benzene, the extract thus made was filtered, and the phosphorus was estimated in the filtrate after the solvent had been evaporated off. S. B. S.

Normal and Pathological Alteration in the Lens of the Eye. ADOLF JESS (*Zeitsch. Biol*, 1913, **61**, 93—142).—During life there is an increase in the weight, the protein, and the water of the crystalline lens, and to a smaller degree in the substances which are soluble in ether. The increase in protein is greater than that in water. Among the proteins, an "albumoid" is more abundant in old age than crystallin, which is the more important in youth.

In senile cataract, the weight, the water, and the protein all decrease, and the loss of water is greater than that of protein; among the proteins crystallin is most diminished; the amount of albumoid is high; the amount of fat, cholesterol, and lecithin are not increased. In traumatic cataract there is no decrease in weight, but both the proteins decrease in amount; fat, cholesterol, and lecithin do not increase, but the relative and occasionally the absolute amount of water usually rises. In senile cataract, the cystine reaction lessens owing to the disappearance of crystallin; the albumoid has no cystine group in its molecule. In old traumatic cataracts the cystine reaction is also negative, owing to the total absorption of crystallin.   W. D. H.

Chemical Investigation of Calcified Aortæ. Franz Ameseder (*Zeitsch. physiol. Chem.*, 1913, **85**, 324—334. Compare A., 1911, ii, 219).—A further series of analyses of calcified aortæ are given with full details of the experimental methods.   E. F. A.

A Pigment in Melanosis of the Mucous Membrane of the Large Intestine. Emil Abderhalden (*Zeitsch. physiol. Chem.*, 1913, **85**, 92—95).—A brown pigment was separated from a melanotic large intestine. An elementary analysis is given, which agreed closely with that of a pigment obtained from tryptophan (A., 1912, i, 521).   W. D. H.

Ferments of the Pancreas. Cesare Serono and Antoniette Palozzi (*Chem. Zentr.*, 1913, i, 1212—1213; from *Arch. Farmacol. sperim.*, 1913, **14**, 501—508).—All the ferments of the pancreas are contained in the glycerol extract, expressed under high pressure, and their activity remains for a long time unimpaired. The proteoclastic activity increases on keeping, that is, with the conversion of trypsinogen into trypsin. In addition to diastase, there is a ferment capable of acting on maltose. The tryptic power is not destroyed by digestion with pepsin. Only the proteoclastic ferment is precipitated by a mixture of sodium chloride and magnesium sulphate.   S. B. S.

Autolysis of the Thymus. M. Kashiwabara (*Zeitsch. physiol. Chem.*, 1913, **85**, 161—172).—Kutscher considered that during autolysis the thymus underwent characteristic changes, especially in the amount of lysine and ammonia formed; the present research does not support this view. The course of autolysis in this organ does not materially differ from that of the liver, and there is no increase in the amount of ammonia formed; in both organs its nitrogen is about 10% of that in the soluble nitrogenous substances. Among the decomposition products, lysine was found, also leucine and tyrosine in small quantities. There are certain differences between liver and thymus in the partition of nitrogen; the mono-amino-acids and proteoses are only about half as abundant in the thymus as in the liver, but the group diamino-acids + peptone + ammonia is twice as great, and the purine bases three times as great.   W. D. H.

Extractive [Mytilitol] in the Valve Muscles of Mytilus edulis. BAREND C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1913, 85, 231—232).—On extraction of the valve muscles of *Mytilus edulis* with water and precipitation of certain impurities with colloidal ferric hydroxide, a substance, $C_6H_{12}O_5,2H_2O$, crystallises from the filtrate; the name *mytilitol* is applied to it. It forms an *acetate*, m. p. 182°, crystallising in microscopic needles, which gives up five acetyl groups on hydrolysis. Mytilitol contains a six-carbon ring, and is regarded as an isomeride of quercitol. The muscles also contain histidine, betaine, taurine, and about 1·5% of glycogen.

E. F. A.

The Influence of Nutrition on the Secretion of Indole and Indican by Healthy Individuals. WACLAW VON MORACZEWSKI and E. HERZFELD (*Biochem. Zeitsch.*, 1913, 51, 314—339).—The amount of substance giving the indole reaction, which is obtained by the distillation of urine, was determined under different conditions of nutrition, and it was found that the amount increased on a diet of fats, of vegetables, and of gelatin, but diminished on a carbohydrate or sugar diet. The addition of proteins caused an increased output as compared with sugars, but a diminished output as compared with fats. No relationship could be found between the indole of the fæces and the indican of urine. The indole of the fæces was estimated both directly as excreted, and after submission to a secondary putrefaction. Fat was found to increase both the indole directly excreted and the amount obtained after secondary putrefaction. The same was found with proteins, whereas carbohydrates had the opposite effect. Vegetables protect proteins from putrefaction, so that the indole directly excreted is diminished, and that obtained by secondary putrefaction is increased to the same extent. The nitrogen and chloride of the fæces are affected in a similar way. At times a relationship between the indican of the urine and the indole of the fæces is to be found, the two rising and falling together; in the case of gelatin, sugar, and fat nutrition, the general metabolism exerts some influence on the amount of indole resorbed from the intestine; but the amount of indican of the urine is regulated by another factor in addition to its resorption from the alimentary tract, namely, the capacity of the organism to destroy the absorbed substance.

S. B. S.

Tryptic Digestion by the Urine. FILIP JOHANSSON (*Zeitsch. physiol. Chem.*, 1913, 85, 72—90).—In the normal urine of man, ox, and horse, no proteolytic enzyme precipitable by caseinogen in an alkaline solution was obtained. In albuminous urine, it is sometimes present. From the urine of the ox, and to a small degree of the horse, the caseinogen precipitate contains an enzyme which favours the proteolytic action of fibrin prepared from ox blood, but has no such action on ox-serum. Trypsinogen is absent from the urine. The substance in question is possibly a kinase.

W. D. H.

Excretion of Glycuronic Acid Mistaken for Glycosuria.
EMIL ABDERHALDEN (*Zeitsch. physiol Chem.*, 1913, **85**, 95—96).—A
case of apparent glycosuria in a child turned out on further
examination to have no sugar in the urine. The reducing pro-
perties were due to free and combined glycuronic acid. The urine
also contained abundant phenol and indoxyl.   W. D. H.

Changes in Voluntary Muscles in Disease R. C. JEWESBURY
and W. W. C. TOPLEY (*J. Path. Bact.*, 1913, **17**, 432—453).—In
wasting diseases the voluntary muscles show varying degrees of
wasting. In acute general diseases there is a hyaline or granular
change, and in a few cases fatty degeneration. In cases of abnormal
carbohydrate metabolism the interstitial fat is increased. Marked
fatty degeneration occurs in diphtheritic toxæmia, certain blood
disorders, and phosphorus poisoning. Glycogen was strikingly
present in all the cases (three in number) of diabetes examined.
Amyloid degeneration was not found at all.   W. D. H.

**Biochemistry of Growth. The Glycogen-content of the
Liver of Rats Bearing Malignant New Growths.** WILHELM
CRAMER and JAMES LOCHHEAD (*Proc. Roy. Soc.*, 1913, B, **86**,
302—307).—Glycogen disappears more rapidly from the liver of
tumour-bearing rats than from that of normal rats. There is no
increased oxidation of carbohydrate material in tumour-bearing
animals, so the result confirms the conclusion arrived at on pregnant
animals, that in growth carbohydrate is used in the synthesis of
protoplasm.   W. D. H.

Nitrogen Content of Malignant Tumours in Man. ROBERT
G. CHISHOLM (*J. Path. Bact*, 1913, **17**, 606—608).—Ten tumours
were investigated; in all cases the nitrogen percentage is lower
in the fresh tumour than in the somatic tissues of the host, with
the exception of the kidney. But reckoned for the dried tissue,
the percentage was lower in four cases only. Cramer and Pringle
found that the percentage of nitrogen coagulable by alcohol was
low in tumour tissue; the variable results on this point obtained
in the present research appear to be due to post-mortem changes.
                                                     W. D. H.

. **Action of Diuretics in Experimental Nephritis.** ARTHUR
E BOYCOTT and JOHN H. RYFFEL (*J. Path. Bact.*, 1913, 17, 458—501).
—After the convoluted tubules are put out of action by uranium
nitrate, secretory diuretics, such as caffeine, fail to produce
diuresis; so also do mechanical diuretics, such as Ringer's fluid. In
the early stages of uranium nephritis, the urine produced is small
in amount, and contains less chlorides than normal. Caffeine urine
contains less chlorides than that produced by Ringer's solution or
5% sodium chloride solution. Uranium causes glycosuria.
                                                     W. D. H.

**Action of Radium Emanations on the Respiratory
Exchange.** J. VON BENCZÚR and DIONYS FUCHS (*Chem. Zentr.*, 1913,
i, 1444; from *Zeitsch. exp. Path. Ther.*, 1913, 12, 564—567).—Doses,

even one hundred times greater than the ordinary therapeutic dose of radium emanation, have only a slight effect in increasing the gaseous exchange, and do not affect the combustion processes taking place in the organism.   S. B. S.

Behaviour of Lecithin towards Radium Emanation and Thorium-X. CARL NEUBERG and LÁSZLO KARCZAG (*Chem. Zentr.*, 1913, i, 1356 ; from *Radium in Biol. Heilkunde*, 1913, **2**, 116—122) —Different authors have assumed that the hæmolytic action of radium emanation and thorium-X is to be referred to a lecithin scission in the red corpuscles. It is found, however, that no hydrolysis takes place when solutions of the active substances are mixed with lecithin emulsions. The acidity does not rise, neither do the solutions differ in colour, odour, or consistence from the ordinary aqueous solutions.   J. C. W.

Burgi's Law of the Combined Action of Drugs. BÉLA VON ISSEKUTZ (*Pflüger's Archiv*, 1913, **151**, 456—478. Compare A., 1912, ii, 667).—When two narcotics are introduced into the organism at the same time, or within a short interval, the combined effect is often greater than the sum of the effects of each individual drug. This increased effect is, according to Burgi, greatest when the drugs have different cell receptors. This theory is adversely criticised in some detail by the author, who illustrates his arguments by numerous examples, both from his own experience and by quotations from the results of other workers. He draws the conclusion that it is difficult, if not impossible, to formulate any law which will explain the combined action of two drugs administered simultaneously.   S. B. S.

Action of Adrenalin on the Respiration. DIONYS FUCHS and NIKOLAUS RÓTH (*Chem. Zentr.*, 1913, i, 1443 ; from *Zeitsch. exp. Path. Ther.*, 1913, **12**, 568—571).—In experiments on men, similar results were obtained to those in the case of animals, namely, an increase in the volume in respiration. In man, however, there was no increase of frequency, as was observed in the case of animals.   S. B. S.

Colchicine and its Derivatives. HERMANN FUHNER (*Arch expt. Path. Pharm.*, 1913, **72**, 228—238).—The activity of some of Windaus's derivatives of colchicine was compared with that of the parent substance. Colchiceine, in which only one of the enolic methoxy-groups of colchicine is saponified, is much less active than the methyl ether, colchicine. If the hydroxyl group is methylated, the original toxic value of colchicine is reached, or nearly so. Replacement of the acetyl group in this by benzoyl reduces the activity to one-tenth of that of colchicine. Oxycolchicine, obtained by oxidation with chromic acid, has on frogs an action resembling that of veratrine, but has no action when given to mammals.
                                                W. D. H.

The Influence of Cholesterol on Hæmolysis. G. JAHNSON-BLOHM (*Zeitsch. physiol. Chem*, 1913, **85**, 59—67).—The inhibitory

influence of cholesterol on the hæmolytic action of saponin, which was discovered by Ransom, was attributed by Windaus to the hydroxyl group of the former substance, and other views have been advanced to explain it. In the present experiments saponin and soaps were employed as hæmolytics, and the inhibiting action of cholesterol was confirmed; it is specially great if the temperature is raised, and increases with the time cholesterol is allowed to act. In saponin-hæmolysis an irreversible process between the red corpuscles and cholesterol occurs. In soap hæmolysis the action is less marked, and the explanation not so clear.

W. D. H.

The Influence of Cyanogen Gas on the Organism. JEAN LOUIS BURCKHARDT (*Arch. Hygiene*, 1913, **79**, 1—24).—When cyanogen, in concentrations much below 0·1 mg. per litre of air, is inhaled by cats, it has no ill effects; in concentrations of 0·1 mg. per litre, it can be inhaled for half an hour without danger. When the concentration reaches 0·2 mg. per litre, it acts toxically within a few hours. Rabbits are less susceptible, and can tolerate concentrations of 0·4 mg. per litre; for these animals the toxic concentration lies between 0·6 and 0·8 mg. per litre. The symptoms are irritation of the mucous membrane, difficulty in respiration, and convulsions; death results from paralysis of the respiratory centre. The symptoms are apparently those of hydrogen cyanide poisoning, the cyanogen reacting in the organism according to the equation $(CN)_2 + 2KOH = KCN + KCNO + H_2O$. If this takes place, 1 mg. cyanogen must have the same toxic action as 1 mg. hydrocyanic acid; the latter is, however, according to Lehmann and his pupils, much more toxic. It is probable, therefore, that other secondary reactions take place.   S. B. S.

The Physiological Action of Fraxin and its Behaviour in the Organism. GIOVANNI B. ZANDA (*Chem. Zentr.*, 1913. i, 1779; from *Arch. Farmacol. sperim.*, 1913, **15**, 117—121).—Fraxin has small physiological action, and a dog can tolerate 2 grams per kilo. of body-weight without ill effects. It has no appreciable influence on blood-pressure or temperature, and the greater part is excreted unchanged within twenty-four hours. To the mouse, it is relatively non-toxic, but it shows a slight action on the activity of a frog's heart.   S. B. S.

Anæmia Produced by the Hæmolysin from Streptococci. J. W. McLEOD and J. W. McNEE (*J. Path. Bact.*, 1913, **17**, 524—537). —Rabbits vary in their susceptibility to streptolysin. Hæmoglobinæmia and hæmoglobinuria are produced, and the hæmolytic property of the filtrate is closely related to its toxicity. Incubation at 37° destroys toxic and hæmolytic properties. The bone marrow hypertrophies in long experiments, and changes were also noted in liver, kidneys, and spleen. Repeated injections produce increased susceptibility and no immunity. The hæmolysis *in vivo* is much less than *in vitro*.

W. D. H.

Degradation of β-Ketonic Acids in the Animal Organism. LEO HERMANNS (*Zeitsch. physiol. Chem.*, 1913, **85**, 233—240).— It is uncertain whether, on decomposition of aliphatic acids in the organism, ketonic or acid intermediate compounds are formed. It is shown that ethyl phenylacetoacetate is decomposed into benzyl methyl ketone and hippuric acid. The ketone at first formed is converted into benzoic acid. When the ketone is administered to dogs, hippuric acid is recovered.

On subcutaneous injection of ethyl benzylacetoacetate, hippuric acid is formed in quantity, and only traces of phenylethyl methyl ketone. This ketone, when administered alone, yields exclusively phenaceturic acid. In this case, therefore, there is acid decomposition in contrast with the ketonic decomposition in the case of the phenyl ester.

Ethyl phenylpropylacetoacetate under similar conditions gives a good deal of hippuric acid, and traces of phenylbutyl methyl ketone.

When phenylbutyl methyl ketone is administered, only phenaceturic acid is obtained in the urine. The ketone is decomposed between the carbonyl and the methylene carbon, and phenylbutyric acid is formed : $C_6H_5 \cdot [CH_2]_4 \cdot CO \cdot CH_3 \rightarrow C_6H_5 \cdot [CH_2]_3 \cdot CO_2H$. The ester, on the contrary, forms phenylvaleric acid :

$$CH_3 \cdot CO \cdot CH \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2Et \rightarrow C_6H_5 \cdot [CH_2]_4 \cdot CO_2H.$$
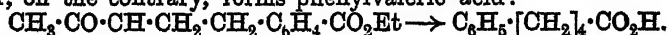
The phenyl group in ethyl phenylacetoacetate has thus an abnormal influence.

The normal formation of acetone in the body is due to similar secondary reactions. Normally, acetoacetic acid is degraded to acetic acid, but under pathological conditions the secondary reaction predominates and acetone is formed. The degradation of the fatty acids accordingly does not take place with the formation of ketones, but there is an elimination of two carbon atoms.

<div align="right">E. F. A.</div>

The Influence of Salvarsan and Neosalvarsan on the Circulation and on the Kidneys of Healthy and Diseased Animals. ALWENS (*Arch. expt. Path. Pharm.*, 1913, **72**, 177—223). —Intravenous injection of salvarsan causes nephritis. Its toxicity increases not only with the dose given, but with the concentration; the histological appearances of the kidneys are described in detail; the nephritis is a vascular one, analogous to that produced by arsenic and cantharides. An immediate result of the injection, if made rapidly, is a fall in blood-pressure. Neosalvarsan produces clinically no nephritis, and in animals the nephritis produced by long-continued use of the drug is less marked; so also is the fall in blood-pressure. In animals which already have nephritis from other causes, the condition is intensified by very small doses of salvarsan, and in cases where the heart is diseased, the action of salvarsan on the circulation is most unfavourable.   W. D. H.

The Relationship of Strophanthin Action and the Intensity of the Heart's Action. VIKTOR WEIZSACKER (*Arch. expt. Path.*, 1913, **72**, 282—294).—It was proved in experiments

on the frog's heart that the action of strophanthin takes place more rapidly the more quickly the heart is beating. In the resting heart, the drug is not completely inactive. The rate of beat being constant, rise of temperature increases the velocity of the action of strophanthin.   W. D. H.

The Resistance of Different Animals Towards Arsenic. M. WILLBERG (*Biochem. Zeitsch.*, 1913, **51**, 231—252) —The following are the tolerated doses of potassium arsenite, expressed in mg. per kilo. of body-weight. For pigeons, less than 0·012 (subcutaneous); mice, 0·0156—0·0176 (subcutaneous); hedgehog, 0·01—0·014 (subcutaneous); rabbits, 0·008—0·01 (subcutaneous); dogs, 0·007 (subcutaneous or intravenous); guinea-pigs, 0·009 (subcutaneous); cats, 0·005—0·006 (subcutaneous); hares, more than 0·005 and less than 0·008 (subcutaneous); snakes, 0·012. The corresponding doses for arsenious acid are: For pigeons, 1·786 (per os); rabbits, 0·015 (per os); dogs, 0·03 (per os); hens, less than 0·06 (per os). It is noteworthy that the tolerance by man is less than by any of the above animals, which is probably due to the more highly developed nervous system. When arsenic is administered by the mouth, animals are to a large extent protected from the poisonous action by vomiting.   S. B. S.

Lipoids which Resemble Lecithin in Forming Hæmolysins along with Cobra-venom. JOHN CRUICKSHANK (*J. Path. Bact.*, 1913, **17**, 619—622).—A number of substances were obtained from the alcoholic extracts of egg-yolk, heart, liver, and kidney, which differ from lecithin. They are all soluble in water, and with one exception in ether. They are precipitated from the ethereal solution by acetone. They all form hæmolysins along with cobra-venom.   W. D. H.

Action of the Lecithins on the Processes of Poisoning in Higher Animals. E. HANSCHMIDT (*Biochem. Zeitsch.*, 1913, **51**, 171—192).—Lecithin by itself exerts no toxic action on animals, which can tolerate large doses, whatever method of administration is adopted. If injected together with curare, strychnine nitrate, ethyl alcohol, chloral hydrate, veronal, or morphine, it inhibited the action of these drugs. It increased, however, the toxic action of ricin. In the case of phosphorus poisoning, the effect of the lecithin appears to depend on the weight of the substance administered, smaller doses having apparently a beneficial, and larger doses a harmful, effect. The general condition of the animal and its body content in lipoids appears also to have some effect in this case.   S. B. S.

Poisoning by Methyl Alcohol. FRANCESCO OLIVARI (*Chem. Zentr*, 1913, i, 1780; from *Arch. Farmacol. sperim*, 1913, **15**, 83—96).—The toxicity of crude and pure methyl alcohol for frogs, mice, and guinea-pigs was investigated. In the case of the pure products, the minimal lethal doses were: for frogs, $16\cdot2^0/_{00}$; for

mice, $11\cdot5^0/_{00}$; and for guinea-pigs, $9\cdot5^0/_{00}$ of the body weight; the corresponding numbers for the crude acid product were 10·0, 7·5, and $6^0/_{00}$; and for the crude basic product, 8·6, 6·8, and $5\cdot5^0/_{00}$. A scheme is given for the forensic examination of drinks, and animal organs in which wood-spirit is suspected. The liquid is acidified with phosphoric acid, and the volatile acids, etc., are distilled off, whilst the bases, pyridine, amines, etc., remain in the residue. The distillate containing the acids is neutralised, and again distilled, the salts of the acids remaining behind, the aldehydes, etc., distilling over. These are fixed by m-phenylenediamine hydrochloride, and the mixture is distilled, when acetone and methyl alcohol distil over, and are estimated in the distillate. If the mixture is saponified before these treatments, a conception can be formed as to the quantity of esters present from the amount of alcohol in this distillate. Finally, ethereal oils can be extracted by mineral oils (b. p. 140—230°), and separated from the higher alcohols by fractional distillation. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Formation of γ Aminobutyric Acid from α-Glutamic Acid by Micro-organisms. EMIL ABDERHALDEN, GEORG FROMME and PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1913, 85, 131—135).—Whereas Ackermann (A., 1910, ii, 1089) identified γ-aminobutyric acid amongst the bacterial decomposition products of d-glutamic acid, Abderhalden and Kautzsch (A., 1912, i, 952) were unable to confirm this. It is now found that γ-aminobutyric acid is formed when a mixture of glutamic acid, dextrose, Witte's peptone, and inorganic salts is incubated with decomposing pancreatic tissue. Success depends on the presence of the proper micro-organism; the mixture contained various yeasts, together with Diplococci and Staphylococci. E. F. A.

Methods in Soil Bacteriology. VI. Ammonification in Soil and in Solution. FELIX LÖHNIS and HENRY HAMILTON GREEN (*Centr. Bakt. Par.*, 1913, ii, 37, 534—562).— A critical study of the factors affecting ammonification and nitrification of blood meal, flesh meal, and horn meal under laboratory conditions. Where the tests are carried out in solution and under aerobic conditions, the quantity of material does not appear to influence the rate of ammonification. Under anaerobic conditions there is a marked retardation of the process, due possibly to an accumulation of bacterial metabolic products. It is suggested that in the initial decomposition of flesh meal and horn meal in shallow layers of liquid, aerobic and anaerobic organisms play perhaps an equally

important part, but that aerobic organisms are concerned more actively with the later stages of ammonification Under aerobic conditions, and with larger quantities of material, considerable amounts of ammonia may volatilise from the cultures, or undergo assimilation by bacteria. The decomposition of horn meal and blood meal is much more rapid in soil than in solution. When, however, soil tests in deep layers at full saturation are compared with solution tests in shallow layers, ammonification is faster in solution than in soil, and this would seem to indicate aeration as being one of the chief factors in determining the rate of decomposition in soils. The three materials used show differences among themselves in the rate of decomposition, and this varies again according as to whether the tests are made in solution or in soil. The conclusion is drawn that solution tests seem to afford more information concerning the nature of the materials used as sources of nitrogen.

Nitrification is not registered in solution in the presence of any of the materials, but in soil tests it keeps pace with ammonification provided that aeration is liberal, and that the quantity of ammonia formed is not excessive.   H. B. H.

The Oxidation of Thiosulphates on Bacterial Filters. WILLIAM T. LOCKETT (*J. Soc. Chem. Ind.*, 1913, 32, 573—581).— It has already been observed that phenol and thiocyanate undergo oxidation on bacterial filters (Fowler, Ardern, and Lockett, A., 1911, ii, 139). In the present investigation, thiosulphate solutions were passed repeatedly through filters, consisting of stoneware pipes 24 in. long, cemented at one end and filled with clinkers. The amount of change in the solution was determined by an estimation of the oxygen absorbed from acid permanganate solution, and of the residual thiosulphate by $N/80$-iodine. It was found that solutions up to 0·5% concentration (expressed as $Na_2S_2O_3$) can be oxidised; the resulting solution is acid, and the addition of alkali accelerates the rate of oxidation. The thiosulphate is oxidised finally to sulphate, but tetrathionate and pentathionate, with occasional traces of trithionate, are intermediarily produced.

In an extension of the investigation to the thionic acids, it was first shown that the usual tests are applicable with but few exceptions to thionate solutions of 0·1 and 0·02% concentration. With the exception of the dithionates, all the thionates undergo oxidation in this manner; potassium trithionate is oxidised to sulphate with intermediate formation of a considerable quantity of tetrathionate; potassium tetrathionate gives sulphate with a little pentathionate, whilst potassium pentathionate is directly oxidised to sulphate.

The conclusion is drawn that the oxidation is due to bacterial agency assisted by the physical and chemical properties of the filtering medium.   D. F. T.

The Products of the Putrefaction of *l*-Aspartic Acid. New Method of Detecting β-Alanine EMIL ABDERHALDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1913, 85, 112—130).—On putrefactive

decomposition of *l*-aspartic acid, succinic, propionic, and formic acids are formed (compare Neuberg and Cappezzuoli, A., 1909, ii, 691). These acids are easily separated by the ester method, as the acid esters may be extracted with ether from the ester hydrochlorides of the amino-acids.

Emphasis is laid on the necessity of carrying out putrefactive decomposition experiments with a single known organism or a mixture of known organisms. β-Alanine obtained by Ackermann (A., 1911, ii, 757) from aspartic acid could not now be identified. It is recognisable in the very smallest quantity by conversion into ethyl acrylate, which has a characteristic odour, and when added to a putrefaction experiment it is easily identified in this manner. Pure cultures of the five micro-organisms present were incubated separately with aspartic acid. In no case was β-alanine formed.

E. F. A.

Reaction Phases of Alcoholic Fermentation. HANS VON EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1913, 85, 192—208).—It is shown generally that, when sugar is fermented in presence of phosphate, the relation between the amount of carbon dioxide liberated and the phosphate fixed throughout the whole course of the change is that expressed by Harden and Young's equation, namely, $2C_6H_{12}O_6 + 2PO_4HR_2 = 2CO_2 + 2C_2H_6O + 2H_2O + 2C_5H_{10}O_4(PO_4R_2)_2$. This expression by no means explains the mechanism of fermentation or the part played in it by the individual enzymes.

Fermentation begins with the conversion by means of an enzyme of the hexose sugars into a carbohydrate, which can be esterified with phosphate. The development of carbon dioxide which accompanies this esterification is checked by an excess of phosphate. The fermentation controlled by phosphate is accelerated by the presence of lævulose. Both hexose diphosphate and triosemonophosphate are formed. The enzymatic hydrolysis of the hexose phosphate ester studied by Harden and Young is materially retarded by the presence of toluene. All the foregoing facts must be taken into consideration in any explanation of the fermentative changes.

E. F. A.

Invertase Reaction of Mixed Yeast Cultures. ALBERT J. J. VANDEVELDE and A. VANDERSTRICHT (*Biochem. Zeitsch.*, 1913, 51, 388—397).—The invertase action of mixed cultures lies generally between that of the varieties forming the mixture, which is in contrast to the effect observed with certain mixed cultures, on the alcoholic fermentation, where a mixture exerts a favouring action.

S. B. S.

Reduction of Acetaldehyde by Yeast Juice. S. KOSTYTSCHEV and ELISE HÜBBENET (*Zeitsch. physiol. Chem.*, 1913, 85, 408—411. Compare A., 1912, ii, 860).—An extract of dried yeast (maceration juice) is proved to reduce methylene-blue to the colourless state, and also acetaldehyde to alcohol, both in the presence and in the

absence of sugar. The active hydrogen in this case is probably formed in the same way as during zymase fermentation. E. F. A.

Are Moulds Able to Form Volatile Substances from Antimony Compounds? ERICH VON KNAFFL-LENZ (*Arch. expt. Path. Pharm.*, 1913, 72, 224—227).—The moulds investigated are not able to form volatile antimony compounds. In this there is a difference between antimony and the similar elements arsenic, selenium, and tellurium. The possibility that chronic antimony poisoning is due to the formation of volatile substances is excluded.
W. D. H.

Nature of the Osmotic Optimum in Biological Processes. ALFRED GUILLEMARD (*Compt. rend.*, 1913, 156, 1552—1554).—A theoretical paper explaining results obtained in the culture of *Aspergillus niger* under various conditions. The living matter absorbs metallic compounds necessary for its physico-chemical constitution, the rate of formation of plant tissue following a curve which presents an optimum for a certain density with respect to the properties of the metal experimented with. The osmotic optimum occurs with most chemical substances in biological reactions. The amount of substance which favours it is the "excitation" dose, and precedes the "toxic" dose. W. G.

Replacement of Zinc by Copper in the Culture of Aspergillus niger CHARLES LEPIERRE (*Compt. rend.*, 1913, 156, 1489—1491. Compare this vol., i, 326, 327).—Like cadmium, glucinum, and uranium, copper can replace zinc in the culture of *Aspergillus niger*. Added in the form of its sulphate, the weight of crop is normal if the amount of copper does not exceed 1 in 500,000, but the growth is retarded. If the amount rises to 1 in 1000, growth ceases. Sporulation takes place only if the copper present does not exceed 1 in 10,000. W. G.

The Assimilation of Guanine and Guanidine by Moulds. ALEXANDER KOSSOWITZ (*Chem. Zentr.*, 1913, i, 1297; from *Zeitsch. Gahrungs physiologie allg. landw. techn. Mykologie,* 1912, 2, 84—86).— Guanine could be used by a large number of moulds as a source both of carbon and nitrogen. These include *Botrytis bassiana, Penicillium glaucum, Mucor γ-Boidin, Cladosporium herbarum, Phytophthora infestans, Penicillium brevicaule, Aspergillus glaucus* and *A. niger,* and *Isaria farinosa.* Guanidine, as carbonate, chloride, nitrate, or thiocyanate, could be used as a nitrogen source by all moulds. S. B. S.

Enzymatic Hydrolysis of Hippuric Acid by Mould Fungi. ARTHUR W. DOX and RAY E. NEIDIG (*Zeitsch. physiol. Chem.*, 1913, 85, 68—71. Compare A., 1909, i, 861; ii, 510).—Some characteristic mould fungi—three Aspergillus and three Penicillium species— were grown for periods of one, two, three, and four weeks in a nutrient solution consisting of sucrose, tartaric acid, and inorganic

salts. The mycelium was removed, ground with glass, the juice expressed, and its action on hippuric acid tested, the formation of glycine being detected by means of titration with formaldehyde. In most cases nearly complete hydrolysis was observed independently of the age of the culture. There is very little secondary action converting glycine into ammonia. Taka-diastase (made from *Aspergillus oryzae*) has a similar hydrolytic action on hippuric acid.
E. F. A.

The Penetration of Different Forms of Nitrogen in Plants; Phenomena of Adsorption. D. CHOUCHAK (*Compt. rend.*, 1913, **156**, 1696—1699. Compare Pouget and Chouchak, A., 1912, ii, 796, 975).—The roots of young wheat plants deprived of vitality by immersion in boiling water for thirty minutes retain the property of adsorbing and fixing nitrogen in diffeernt mineral and organic forms. This property is due to the presence of certain substances not removed by boiling water, but removed by boiling alcohol. This power of adsorbing different nitrogenous compounds, at the same molecular concentration, varies according to the nature of the compound, and for the same form of nitrogen, the amount of nitrogen adsorbed varies, within certain limits, directly with the concentration of the surrounding medium with respect to nitrogen. The ratio of the concentration of adsorbed nitrogen in the roots to that of the nitrogen remaining in the liquid is always greater than unity.
W. G.

The Absorption of Different Forms of Nitrogen by the Plant; Influence of the Medium. D. CHOUCHAK (*Compt. rend.*, 1913, **156**, 1784—1787. Compare preceding abstract).—The adsorbing power of the exterior layer of dead roots, and the rate of absorption or diffusion in the living plant, for the same concentration in nitrogen, is considerably modified by the presence of such salts as magnesium sulphate, sodium chloride, etc., and the effects produced by a number of these have been studied. They do not act in the same manner, but by their action on dead roots and on living plants they arrange themselves in the same order. In a mixture of two or more salts, they may help or be antagonistic to one another. In many cases the adsorption of nitrogen is very considerably increased, sodium chloride having a beneficial effect.
W. G.

The Significance of Lipoids for the Formation of Bio-electrical Differences of Potential in Certain Plant Organs. JACQUES LOEB and REINHARD BEUTNER (*Biochem. Zeitsch.*, 1913, **51**, 288—299).—The bio-electrical differences of potential already described by the authors at the undamaged surface of certain plant organs (apple, etc.) are qualitatively and quantitatively almost identical with that at the interface of an aqueous solution, and a solution of phosphatides in guaiacol, *m*-cresol, and amyl alcohol, and a guaiacol extract of apple behaves in this respect exactly like the undamaged organ itself. The solvents themselves without the

phosphatide have practically no action. Fatty acids which are insoluble in water, such as oleic and palmitic acids, show the same effect towards the varying concentrations of the aqueous salt solutions as the living organ. They behave, however, differently towards different concentrations of acids. The bio-electric action of the organs is not due therefore to fatty acids, neither is it due to cholesterol, the electromotor effects of which are quite different to those of the living organ. Solid proteins, such as coagulated egg-white or gelatin, also act in a different way. The bio-electric effects of the living organ are therefore ascribed to the presence of phosphatides or some similar insoluble substances. Cephalin and lecithin were used in the experiments in chains, which were constituted in the following way: Hg | HgClM/1KCl | Guaiacol solution | KCl in varying concentrations | M/KClHgCl | Hg.   S. B. S.

The Influence of Anæsthetics on the Potential Difference at the Surface of Living Animal and Vegetable Tissues. JACQUES LOEB and REINHARD BEUTNER (*Biochem. Zeitsch.*, 1913, **51**, 300—306).—The addition of alcohol or ether to the aqueous phase diminishes the difference of potential at the interface of a living organ and an aqueous solution. The action is a reversible one. The quantities necessary to produce an effect are considerably larger than those necessary for the production of narcosis. A similar diminution of difference of potential is produced by the addition of alcohol or ether to the aqueous phase at the interface of an aqueous solution and a solution of oleic acid or lecithin in guaiacol. The action is due to the entrance of some ether into the non-aqueous phase. A similar action was not observed on the addition of an indifferent non-electrolyte, such as dextrose, to the aqueous phase.   S. B. S.

The Part Played by the Surface Tension and by Lipoids in the Living Cell. HORACE M. VERNON (*Biochem. Zeitsch.*, 1913, **51**, 1—25).—Exosmosis of tannin from vegetable cells, caused by various narcotics, is apparently not a mere surface-tension phenomenon, as Czapek assumes. According to this observer, the substances cause exosmosis in those concentrations which reduce the surface tension of water/air to 0·685. Out of the twenty-nine substances investigated by Czapek, seven produce exosmosis in concentrations in which the surface tension varies between 0·82 and 0·998. The concentrations, according to the author, more nearly correspond with those which produce narcosis in tadpoles and hæmolysis of blood-corpuscles. The narcotics appear therefore to exert their action owing to their solubility in lipoids, according to the Overton theory. The part played by the lipoids in animal cells can be investigated by determining the concentration of the various substances which inhibit the action of indophenoloxydase, an insoluble ferment which only acts, according to the author, when the lipoids are intact. It is now found that the concentrations of narcotics which are just sufficient to inhibit this ferment action

are about twice as strong as those which cause exosmosis of tannin from *Echeveria* cells. The actual ratios vary between 0·9 and 2·8 for the seventeen substances investigated. As the concentrations varied between 1 and 720, the closeness of these ratios is striking. Colloidal sodium oleate acts in the same concentrations on *Echeveria* as on oxydase, whereas saponin acts on the oxydase in 1/40 of this concentration. Acids act on oxydase in concentrations corresponding more or less with the electrical conductivity of this solution, and there is a crude parallelism between these values and their hæmolytic action. S. B. S.

Carbohydrates of Vegetables ERNST BUSOLT (*J. Landw.*, 1913, **61**, 153—160).—The sap of French beans (3000 c.c.), when kept for a week, yielded 9·3 grams of pure mannitol. No mannitol was found in the sap when quite fresh, or in sap which was at once sterilised by boiling and then kept for a week.

Cauliflower (1300 grams), without the stalk, yielded 7·9 grams of pure mannitol, which is supposed to have been present originally. It is, however, possible that the mannitol was produced during the evaporation of the sap. N. H. J. M.

Simple Vegetable Bases. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, **85**, 372—391).—Emphasis is laid on the fact that the plant betaines are to be regarded as the simplest alkaloids formed from the amino-acids by exhaustive methylation.

The presence of glycine betaine and of choline in the alcoholic extract of oat seeds is established. In the phosphatide from oats, colamine (aminoethyl alcohol) but no betaine is present.

Glycine betaine may be identified as platinichloride. This salt undergoes a characteristic change when left in contact with its mother liquors.

Aminoethyl alcohol reacts quantitatively with nitrous acid, and may be estimated in this way. Since choline does not react with nitrous acid, the presence in it of 1% of colamine may be detected. Colamine is incompletely precipitated by phosphor-tungstic acid.

An investigation of the bases in areca nuts leads to the following formulæ being suggested:

$$\text{Guvacine, } C_6H_9O_2N = CH_2 \! \! <^{CH_2 \cdot CH_2}_{N = CH} \! \! > \! CH \cdot CO_2H.$$

$$\textit{iso}\text{Guvacine, } C_6H_9O_2N = CH_2 \! \! <^{CH_2 \cdot CH_2}_{NH - CH} \! \! > \! C \cdot CO_2H.$$

$$\text{Arecaine, } C_7H_{11}O_2N = CH_3 \! \! <^{CH_2 - CH}_{CH_2 \cdot NMe} \! \! > \! CH \mid {}^{- \; - \; CO}_{\quad \; O}.$$
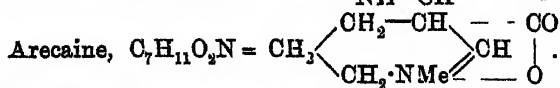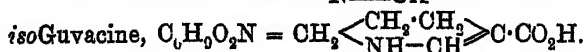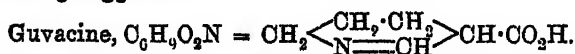
These differ from the formulæ suggested by Jahns. E. F. A.

Formation of the Anthocyan Pigments of Plants. IV. The Chromogens. FREDERICK KEEBLE, E. FRANKLAND ARMSTRONG, and W. NEILSON JONES (*Proc. Roy. Soc.*, 1913, *B*, **86**. 308—317. Compare A., 1912, ii, 673; this vol., i, 325).—Flowers of any colour

variety of Brompton stocks, when treated with alcohol, lose their colour rapidly. The original colour is regained when the decolorised petals are placed in water, the recovery being rapid when the water is heated. The phenomenon is a general one, and it is also shown by the vegetative parts of plants. The brown wall-flower, which contains a mixture of purple anthocyan and yellow plastid colour, recovers purple. The power of recovering the original colour serves as a means of distinguishing anthocyan from plastid pigments. The recovery of the pigment is shown to be due to the oxidation of a chromogen.

The decolorisation is due to the activity of a reducing agent, which is extracted by alcohol. This is resistant to high temperatures, as the alcohol may be evaporated to dryness, and the residue taken up in water; it then contains an active reducing agent. This agent prevents the action of ·bran peroxydase on benzidine, whilst, when added to the blue solution resulting from the interaction of bran peroxydase, hydrogen peroxide, and benzidine, it brings about the decolorisation of the blue. Quinol has a similar effect, but not formaldehyde.

The flower petals contain a much larger quantity of chromogen than is used in the natural flower, as the colour may be removed and recovered several times. The amount of active water present in the cells determines the direction in which the pigment producing reaction shall go; as the amount of water decreases, the reducing agents become active and the oxydases inert.

The activity of α-glucase ceases in 60% ethyl alcohol and in 40% methyl alcohol. The activity of emulsin falls rapidly in alcohols up to 40% strength; in solutions with from 40 to 90% of alcohol the activity is proportional roughly to the amount of water present. Oxydase action ceases in about 70% alcohol, but in the plant cell the chromogens may undergo oxidation, even in 95% alcohol.

E. F. A.

Formation of the Anthocyan Pigments of Plants. V. Chromogens of White Flowers. W. NEILSON JONES (*Proc. Roy. Soc.*, 1913, *B*, 86, 318—323. Compare Keeble and Armstrong, A., 1912, ii, 673).— Lack of colour in recessive white flowers may be the consequence, not of the absence of an essential constituent of the colour-producing mechanism, but of the failure of these constituents to come together and interact with one another. White flowers of *Lychnis coronaria* contain a chromogen which gives rise to a reddish-brown pigment on oxidation. The chromogen may be extracted by treatment with absolute alcohol; it reacts with the peroxydases in other plants in presence of hydrogen peroxide to form the brown pigment, and can thus be used in the same way as benzidine to demonstrate the distribution of oxydase. In *Lychnis* the natural conditions are never such as to allow any interaction between oxydase and chromogen. On treatment with alcohol or a similar hormone, the barrier is removed by the destruction of the plasmatic impermeability, and pigment is formed. The following types of white flowers have been demonstrated: (1) Those which contain

an oxydase and a chromogen, for example, *Lychnis coronaria.* (2) Those which contain a peroxydase and a chromogen, for example, *Dianthus,* sp. (3) Those which contain a peroxydase but no chromogen. These give no colour reaction after treatment with chloroform and hydrogen peroxide. (4) Those which contain no peroxydase.   E. F. A.

Variation in the Composition of Water-Trefoil (Menyanthes trifoliata, L.) during a Season's Growth. MARC BRIDEL (*J. Pharm. Chim.,* 1913, [vii], **7.** 529—535. Compare A., 1911, i, 659).—This investigation was carried out on the same lines as were adopted in the case of gentian root (A., 1911, ii, 426), with the exceptions that (1) the carbohydrates hydrolysed by invertase in the water-trefoil are unknown, and (2) that meliatin, unlike gentiopicrin, cannot be isolated and weighed. The proportion of meliatin was therefore estimated by the change in rotation induced by emulsin in an aqueous solution of a dry alcoholic extract of the plant, in which (1) the initial reducing sugar, and (2) the carbohydrates hydrolysed by invertase had already been determined.

The results, tabulated in the original, show that the plant contains most meliatin (0·891%) towards the end of May, and least (0·655%) at the beginning of October. The carbohydrates hydrolysed by invertase are at a minimum (0·950%) at the middle of June, and increase steadily to 2·761% at the beginning of October. As in the case of gentian, it appears that the percentage of glucoside shows little variation, so that this substance cannot be regarded as a reserve material. On the other hand, the carbohydrates are accumulated as reserve materials up to the period at which the fruit ripens, to be used at the resumption of vegetative activity.   T. A. H.

Husks of Buckwheat Seeds. KURT FESSLER (*Zeitsch. physiol. Chem.,* 1913, **85,** 148—155).—The :brown husks of buckwheat seeds are reputed to contain a green pigment not identical with chlorophyll. The poisonous action of the husks towards animals is attributed to the photodynamic action of this pigment. The green pigment has now been studied more in detail and its absorption spectrum recorded; it shows red or brownish-red fluorescence in organic solvents. On keeping, the green colour changes to a yellow or brownish-green.

A yellow xanthophyll pigment is also present, which is closely related to phytosterol. The brown pigment of the husks is identified as a phlobaphen.   E. F. A.

The Fruit of Crataegus macracantha. W. BRUCE ARMSTRONG (*Chem. News,* 1913, [iv], **13,** 280—281).—The fruits yielded 17·98% of sugars, 2·085% of ash, and contained 0·595% of nitrogen and 0·79% of oil. Protein was detected in all the fruits, and Wagner's reagent and the phenolphthalein test indicated that atropine may be present, although no other evidence of this could be obtained.

The ash had the following percentage composition: Al_2O_3 (trace of iron), 6·86; CaO, 13·93; MgO, 12·16; K_2O, 23·80; Na_2O, 37·63; SO_3, 3·09; Mn, 0·10; Cl, 0·15. The sugars present included dextrose and lævulose. Acetic and citric acids were also present, the former due to fermentation.   T. A. H.

The Pharmacognosy of the Manna Ash. GIOVANNI B. ZANDA (*Chem. Zentr.*, 1913, i, 1779; from *Arch. Farmacol. sperim.*, 1913, **15**, 66—82).—Details are given for the preparation of the manna. To separate mannitol from fraxin, the aqueous extract of *Fraxinus* bark is treated with neutral lead acetate, the mixture is filtered, and then basic lead acetate is added. The mannitol in the filtrate can be estimated gravimetrically or polarimetrically. The fraxin is precipitated as a lead compound, which is decomposed by hydrogen sulphide. The product thus obtained is freed from tannic acid by treatment with a small quantity of water and recrystallised from alcohol. The fraxin can be estimated by titration with Fehling's solution after hydrolysis with dilute hydrochloric acid. The mannitol and fraxin contents of various species and of trees from different provinces and in different seasons were also investigated. When the quantity of mannitol is relatively large, that of fraxin is small and vice versa.   S. B. S.

Presence of Gentiopicrin in the Leaf-bearing Stems of Gentiana spp MARC BRIDEL (*J. Pharm. Chim*, 1913, [vii], **7**, 486—492. Compare this vol., i, 434).—The leaf-bearing stems of *Gentiana cruciata*, L., *G. lutea*, L., and *G. asclepiadea*, L., were first examined by Bourquelot's biochemical method, and gave indications of the presence of gentiopicrin. The latter was then extracted from each of these materials. The first-named plant yielded very little, in which respect it resembles *G. pneumonanthe*, the stems of which also contain only a small amount of the glucoside (A., 1910, ii, 887).   T. A. H.

Fruit of American Holly (Ilex opaca). F. F. CARHART and G. H. MILLER (*Chem. News*, 1913, **107**, 243—244).—The dry fruit contained 46·34% of reducing sugars, 8·31% of ash, 0·61% of nitrogen, and 1·5% of oil, as well as oxalic acid and proteins. The reducing sugars include dextrose and lævulose. The percentages of the constituents of the ash are as follows: SO_3, 4·59; Al_2O_3, 10·08; Fe_2O_3, 1·27; CaO, 15·91; MgO, 8·01; P_2O_5, 14·06; K_2O, 17·15; Na_2O, 24·32; MnO, 0·10; Cr, nil. The oil had D 0·9358 and saponification equivalent 303, and appeared to belong to the castor oil group.   T. A. H.

Comparison of the Hydrolysing Diastases of the Latex of Maclura aurantiaca with those of Ficus carica and Broussonetia papyrifera. C. GERBER (*Compt. rend.*, 1913, **156**, 1573—1575).—The latex of *Maclura aurantiaca*, like those of *Broussonetia papyrifera* and *Ficus carica*, merits the name of "vegetable pancreatic juice." Like them, and in the same way as

animal pancreatic juice, it hydrolyses and renders soluble carbohydrates, fat and protein substances, and plays a primary part in the nutrition of the plant. These properties are due to the existence of certain enzymes, the characteristics of which are intermediate between those of the enzymes of the *Broussonetia* and *Ficus*, and place the latex of the *Maclura aurantiaca* between those of these two plants, and nearer to the first than the second.

W. G.

Migration of the Constituents of Maize Grain in Water and Aqueous Solutions. EDMOND POPPE (*Bull. Soc. chim. Belg.*, 1913, 27, 103—109. Compare A., 1911, ii, 428).—Maize grains, when steeped in water or in dilute aqueous solutions of chlorides, nitrates, phosphates, or sulphates, or in saturated solutions of sucrose or sodium chloride, at the ordinary temperature for forty-eight hours, lose but very small amounts of their constituents. If, however, they are steeped in boiling solutions, a large amount of the nutritive substances is removed, and the grains diminish in alimentary value by 36·2%. Dilute solutions of the above-mentioned salts behave as distilled water with respect to the amount of nutrients removed. The ordinary temperature is not sufficiently high to kill the epidermic cells and so destroy their semi-permeability, but this occurs at the higher temperature, and the cell-walls become permeable to all the substances dissolved in the water. W. G.

Some Data on the Ripening of Florida Oranges. F. ALEX. McDERMOTT (*J. Amer. Chem. Soc.*, 1913, 35, 834—837).—A study has been made of the enzymes in the peel of Florida oranges with a view to ascertaining whether any change takes place in their nature or activity at the point at which the fruit becomes sufficiently ripe for consumption. The peel contains peroxydase, catalase, and invertase enzymes, but no oxydases. During ripening, the weight of the peel decreases in relation to the total weight, whilst that of the juice increases about equally in this relation. The total amount of acid in the juice decreases only slightly, but its concentration decreases considerably, whilst the sugar increases both in concentration and total amount. E. G.

Chemical Examination of the Roots of Phaseolus multiflorus, Lam. FREDERICK B. POWER and ARTHUR H. SALWAY (*Pharm. J.*, 1913, [iv], 36, 550—552).—The statement having been made that the roots of this plant (scarlet runner bean) are poisonous, the authors have submitted the roots to a systematic chemical examination, and have isolated a number of definite constituents. Physiological tests of certain of these constituents, and of extracts of the roots, furnished no evidence that the roots are toxic.

An aqueous extract of the roots on precipitation with alcohol furnished a preparation which hydrolysed amygdalin and gave the biuret reaction. No hydrocyanic acid was formed on macerating the ground roots in water.

An alcoholic extract of the roots was mixed with water and

steam distilled, and thus separated into (a) a small amount of brown essential oil, (b) resinous matter, and (c) matter soluble in water. From the last-mentioned portion furan-3-carboxylic acid (compare Rogerson, T., 1912, 101, 1044), allantoin (compare Ackroyd, A., 1911, ii, 308; Titherley and Coppin, A., 1912, ii, 289), an amorphous, glucosidic substance, and a reducing sugar which furnished d-phenylglucosazone were obtained.

The resinous matter was extracted successively with light petroleum, ether, chloroform, ethyl acetate, and alcohol. The material soluble in light petroleum was heated with alcoholic potassium hydroxide, and from the product of this reaction a *phytosterol*, $C_{27}H_{46}O$, m. p. 130°, pentatriacontane, and a *phytosterolin*, m. p. 275° (*acetyl* derivative, m. p. 162°), were isolated, as well as a mixture of solid fatty acids, which had m. p. 55°, and some liquid fatty acids, consisting of oleic, linoleic, and a third acid of lower molecular weight.

From the ether, ethyl acetate, and chloroform extracts nothing definite was isolated, but the second contained some glucosidic material.

The portion insoluble in the foregoing organic solvents, but soluble in alcohol, yielded a glucoside, *phaseosaponin*,

$$C_{50}H_{84}O_{20},7H_2O,$$
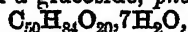
m. p. 238° (decomp.), crystallising in colourless leaflets, and having the properties of a saponin. On hydrolysis by hot dilute hydrochloric acid, this furnished rhamnose (4 mols.) and *phaseosapogenin*, $C_{26}H_{44}O_4$, m. p. 200° (dry, decomp.), which could not be obtained crystalline. A different saponin and sapogenin of the above empirical composition were found by van der Haar in *Polyscias nodosa*, Forst (A., 1912, i, 885).   T. A. H.

Pine Nut Oil. MAXWELL ADAMS and AUGUST HOLMES (*J. Ind. Eng. Chem.*, 1913, 5, 285—287).—The seeds obtained from the cones of the nut pine (*Pinus Monophylla* or *P. Fremontiana*), a tree growing on the Sierra Nevada Mountains, California, yield about 12% of oil having an aromatic odour and agreeable taste; it is light yellow in colour, but becomes colourless on exposure to light. The oil has m. p. −15°, b. p. 305°/60 mm., n_D^{40} 1·4543, saponification number 189·3, iodine number (Hübl) 108, and consists chiefly of olein, together with small quantities of stearin, palmitin, laurin, and linolein.   W. P. S.

Fruit of the "Snowberry" (Symphocarpus racemosus). C. B. SMITH (*Chem. News*, 1913, 107, 266).—The dried fruits contained 4·1% ash, 17·17% sugars, 1·1% of oil, 0·59% nitrogen (=3·68% protein) as well as tartaric and citric acids and a trace of malic acid. No alkaloids were found. The ash had the following percentage composition: SiO_2, 0·78; Fe_2O_3, 2·10; Al_2O_3, 3·15; CaO, 15·11; MgO, 6·30; Na_2O, 8·32; K_2O, 40·26; SO_3, 6·95; P_2O_5, 14·87; Mn, 0·94. The sugars probably included dextrose and lævulose. The oil had saponification value 212·3.   T. A. H.

Imbibition of Strychnos Seed. EDUARD VERSCHAFFELT (*Pharm Weekblad*, 1913, 50, 697—706).—The seed of *Strychnos Nux vomica* has a cuticular layer permeated very slowly by water. The presence of this layer greatly retards the imbibition of the seed, but addition of chloroform, ethyl acetate, and certain other organic substances produces a marked augmentation in the permeability to water, and hence in the velocity of imbibition.   A. J. W.

Occurrence of Barium in Tobacco and Other Plants. JAMES S McHARGUE (*J. Amer. Chem. Soc.*, 1913, 35, 826—834).—Crawford (*Bull.* No 129, *Bur. Plant Indust*, *U.S Dept Agric*) has shown that the poisonous effect of loco-weed (*Astragalus* spp) on cattle is due to the presence of barium, and further work has shown that barium is of common occurrence in plant tissues and soils.

Barium has now been found in tobacco in amounts varying from 0·009% to 0·074% (calculated as $BaSO_4$). Some of the barium can be extracted from the leaves by means of water, and is probably present in combination with organic acids   It is suggested that the occurrence of barium in living cells of the higher plants may indicate that the metal has some metabolic function.   E. G.

Constituents of the Leaves of Zygadenus intermedius.   III. FREDERICK W. HEYL and F. E. HEPNER (*J. Amer. Chem. Soc*, 1913, 35, 803—811) —In an earlier paper (this vol., i, 386) an account has been given of zygadenine, a crystalline alkaloid obtained from the leaves of *Zygadenus intermedius*.   Further investigation of the leaves has shown that in addition to the alkaloid, sucrose, reducing sugars, and dextrin (A , 1911, ii, 326), they also contain the following substances: Quercitin; cerotic acid; a *phytosterol*, m. p. 135°, $[\alpha]_D^{20} -29·5°$, which yields an *acetyl* derivative, m. p. 122—123°; hentriacontane, m. p. 68°; a fat, composed of the glycerides of stearic, palmitic, linolic, oleic, and *iso*linolenic acids; a polyhydric *alcohol*, m. p. 285—288°, of the ipuranol class; and a crystalline substance, m. p. 112—114°, which has not been identified.

The ash from (1) the leaves and tops and (2) the bulbs had the following composition, the first figure in each case referring to (1) and the second to (2): Moisture, 3·79, 2·04; Cl, 0·30, 0·19; CO_2, 18·05, 16·61; sand, 8·31, 7·01; C, 0·71, 0·48; soluble SiO_2, 4·39, 3·55; SO_3, 2·89, 3·33; P_2O_5, 5·03, 8·73; Fe_2O_3, 1 03, 1·08; Al_2O_3, 2·55, 1·08; Mn, traces; CaO, 25·37, 26·48; MgO, 5·34, 5·02; Na_2O, 5·58, 4·68; K_2O, 20·64, 20·35.   E. G.

Acidity in Silage : Method of Estimation   C O. SWANSON, J. W. CALVIN, and EDWIN HUNGERFORD (*J Amer. Chem. Soc.*, 1913, 35, 476—483).—The estimation of acidity in silage is usually carried out on an aqueous extract (compare Hart and Willaman, A , 1912, ii, 1205; Dox and Neidig, this vol., i, 236). A comparison has now been made of the efficiency of water and alcohol as extracting agents, and it has been found that equally uniform results are obtained by means of either solvent, but that the alcoholic extracts always contain a higher percentage of acids than the aqueous. It

therefore follows that some of the acids in silage are soluble in alcohol, but insoluble in water. The quantities insoluble in water vary with different kinds of silage, but are greatest in maize silage.

E. G.

Occurrence of Methyl Alcohol in Fruit Wines   HUGO BAUER and R. ENGLER (*Pharm Zentr.-h.*, 1913, **54**, 445—447. Compare Wolff, A., 1901, i, 110).—Methyl alcohol was found in currant wine; the amount was too small to be of practical importance.

N. H. J. M

The Part Played by Oxydases in the Curly Top Disease of Sugar Beet. HERBERT H. BUNZEL (*Biochem Zeitsch*, 1913, **50**, 185—208) —Leaves of plants with this disease contain two to three times as much oxydase as those of normal plants. No differences could be detected in the roots In beets in which the growth was impeded by other factors, no abnormally high content in oxydase could be detected. The difference in the oxydase content of leaves of different plants is not merely a function of their size, and young and healthy leaves are normal in this respect. Where a normal function of the plants is suppressed, such as the formation of seeds, there is a high oxydase content. The general conclusion is drawn that abnormal disturbances of growth lead to an increased oxydase content of the leaves. Attention is called to similar high oxydase contents in other plant diseases. The general distribution of the oxydases in the various juices of the plant was also investigated The expressed juice of seeds is richest in oxydase; then follow the leaves and roots.

S. B. S

Action of Flowers of Sulphur on the Growth of Sugar Beet. JOSEF URBAN (*Zeitsch. Zuckerind Bohm*, 1913, **37**, 441—444). —Application of flowers of sulphur slightly increased the yield of sugar beet. The sulphur was without effect on the colour of the leaves, and also had no effect on the amount of sugar and the quality of the juice.

N. H. J. M.

The Acids in Honey. ALFRED HEIDUSCHKA and G. KAUFMANN (*Chem. Zentr.*, 1913, i, 1221   from *Südd. Apoth. Zeit.*, 1913, **53**, 118—119).—About half of the volatile acids in honey is represented by formic acid, which was estimated in the steam-distillate and found to compose $0·0037$ to $0·0072\%$ of the substance The non-volatile acids were estimated by the method of Heiduschka and Quincke (A., 1908, ii, 73) with the result: Lactic acid, $0·0225\%$; malic acid, $0·0019\%$; traces of tartaric acid; the merest traces of higher fatty or wax acids; no succinic acid; phosphoric acid, $0·0286\%$ as P_2O_5. This accounts for about one-quarter of the total acidity as measured by $0·1N$-potassium hydroxide. The remainder is largely due to carbon dioxide and to amphoteric substances   J. C. W.

Behaviour of Nitrates in Soils IGNAZ VOGEL (*Landw. Versuchs-Stat.*, 1913, **82**, 158—159. Compare A , 1912, ii, 1200)- The high

and irregular losses of nitrogen previously observed are now shown to be due to absorption of nitrates by the glazed dishes in which the soils were kept. Subsequent experiments showed, however, that light humous soils, kept in thin layers, may lose, in a few days, 10—12% of the nitrates present. The loss of nitrates is now attributed to denitrification, and not to a chemical decomposition of nitrates, or to assimilation. N. H. J. M.

The Behaviour of Acid Amides in the Soil. Samuel L. Jodidi (*J. Franklin Inst.*, 1913, 175, 245—258. Compare A., 1910, ii, 339; 1911, ii, 820).—The author, having previously shown the different forms in which organic nitrogen exists in soils, now describes experiments on the ammonification of acetamide and propionamide when mixed with soil under different conditions; after varying intervals of time these mixtures were distilled with either magnesium oxide or barium carbonate, and the evolved ammonia carefully estimated.

It is found that acetamide and propionamide readily undergo ammonification when mixed with soil, that the rate of transformation is greatly influenced by the chemical structure of the amide, and that the maximum percentage of ammonia obtained from acetamide and propionamide is 83·43% and 75·14% respectively. F. M. G. M.

Fixation of Ammonia by Permutite and Clay Soils. Availability of Permutite Nitrogen for Plants. David J. Hissink (*Landw. Versuchs-Stat.*, 1913, 81, 377—432).—The results of pot experiments showed that oats assimilate nitrogen as ammonium sulphate and as permutite nitrogen about equally well, 70% of both being utilised. The solubility of the two forms of nitrogen in water saturated with carbon dioxide is, however, totally different, permutite nitrogen requiring 1300 to 1400 times as much water as the nitrogen of ammonium sulphate held by a clay soil.

The very slow liberation of ammonia from permutite indicates that the ammonia is partly chemically combined, and not merely held by adsorption. N. H. J. M.

Evolution of Sulphur in Soil; Study of its Oxidation. Ch. Brioux and Marcel Guerbet (*Compt. rend.*, 1913, 156, 1476—1479).—A study of the oxidation of sulphur when introduced into various kinds of soil, with or without the addition of certain other substances. The results show that the oxidation is almost entirely due to microbic action. With garden soil the oxidation is slow at first, but becomes very rapid after the tenth day, the introduction of carbohydrates, such as sucrose and starch, having a marked retarding influence on the rate of oxidation, whilst peptone produces very considerable increase in the oxidation after the fifteenth day. The addition of chalk to a soil poor in lime increases the rate of oxidation by fixing the sulphuric acid formed. The inoculation of sterilised soil by ordinary soil water increases the rate of oxidation by about twenty to sixty times. W. G.

Chemical Causes and Character of the Injurious Effect of Large Amounts of Lime on Peat Soil. GEORG A. RITTER (*Bied. Zentr.*, 1913, **42**, 239—242; from *Fuhling's Landw. Zeit.*, 1912, 593).—The losses of nitrogen which take place when lime and nitrates are applied to peat are attributed to chemical and not to biological action. A very small part of the loss may be due to the production of nitro-compounds from humus; the main cause of the destruction of nitrates is the reducing action of the humus.

The injury to vegetation observed when lime alone is applied in large amounts to peat cannot be due to the destruction of nitrates, since no nitrates are present, but to the increased oxidation of the organic matter and the production of substances, such as oxalic, formic, and acetic acids, etc., which are injurious to plants.
N. H. J. M.

Influence of Humus on the Weathering of Silicates. H. NIKLAS (*Bied Zentr.*, 1913, **42**, 231—232, from *Intern. Mitt. Bodenk.*, 1912, **2**, 214).—The results of experiments in which silicates were kept in contact with peat for seven years, showed that the silicates were only very slightly attacked.   N. H. J. M.

Zeolitic Properties of Ground Phonolite and Lime Trass Manure Compared with some Soil Varieties. ERICH BUSSMANN (*J. Landw.*, 1913, **61**, 97—134).—The ammonia of ammonium chloride is very strongly and chemically absorbed by lime trass; it is strongly absorbed by marsh soil, and well absorbed by phonolite, whilst red soils and loam have respectively only moderate and slight absorptive properties. All the substances adsorb potassium in dilute solutions, and absorb it in strong solutions. Calcium is only notably absorbed by lime trass. Nitrogen as nitrates is not absorbed by any of the substances, and magnesium only by lime trass and marsh soil. Phosphoric acid is 'fixed chemically, most by lime trass, and least by lime.

Under certain conditions the addition of phonolite and lime trass is favourable to the activity of Azotobacter, and consequently induce increased fixation of nitrogen in the soil. The sum of factors which produce this result is, however, still unknown.
N. H. J. M.

Manure Analyses. EILHARD ALFRED MITSCHERLICH and WILH. SIMMERMACHER (*Landw. Jahrb.*, 1912, **43**, 405—435).—A continuation of the author's work on the law of minimum as a logarithmic function (compare A., 1911, ii, 760). Numerous analyses are described, and the results tabulated, from which the author deduces formulæ supporting his theory.   F. M. G. M.

Organic Chemistry.

Formation of Pure Methane from Aluminium Carbide.
ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1913, **11**, 317—319).—The carbide may on treatment with water yield alkali hydroxides, which with metallic aluminium give hydrogen, which in one case amounted to 8% of the gas.   G. D. L.

The Inflammability of Acetylene Mixed with Approximately 30% of Air. MARCEL DELEPINE (*Eighth Inter. Cong. App. Chem.*, 1912, **4**, 25—28).—In a series of experiments on the inflammability of mixtures of acetylene and air in approximately the proportion 70 : 30, an ovoid globe of one litre capacity was used. Electric sparks 2 mm. in length failed to ignite the gas even when the pressure was increased to $1\frac{1}{2}$ atmospheres. An electrically heated platinum wire is more effective than one of iron, for a wire of the latter metal, 2 cm. in length, caused ignition only when the additional pressure was 3·5 cm. and the wire was actually fused. The effect of the extent of the heated surface is indicated by the failure of a platinum wire 10 mm. long and 0·1 mm. in diameter to inflame a mixture under 11·3 cm. additional pressure although the wire fused, whilst a wire 0·2 mm. in diameter and 20—30 mm. long inflamed the gaseous mixture even when the pressure was slightly reduced; the latter wire failed to ignite a similar gaseous mixture enclosed in a lead tube 20 mm. in diameter and 1·4 mm. long. Mercury fulminate is very active in causing ignition, for although 0·005 gram failed to affect a mixture containing 29% of air, 0·01 gram caused inflammation in a mixture containing 28% of air under an additional pressure of 1 cm.; if the air is reduced to 23%, however, the pressure must be increased by more than 9 cms. before ignition is caused by this quantity of fulminate.

The initiation of the combustion is believed to be due to the primary decomposition of the acetylene giving hydrogen which forms a more combustible mixture with the air; the combustion of the new mixture then induces the inflammation of the remaining gas. It is suggested that the decrease in inflammability in the lead tube used above is due to the rapid mixing of the hydrogen and air being checked.   D. F. T.

Action of Acetylene on Some Copper Compounds: New Cupro-Acetylene Compounds. FELIPE LAVILLA LLORENS (*Anal. Fis. Quim.*, 1913, **11**, 320—327).—When pure acetylene is allowed to act on a 10% solution of copper sulphate, to which is added 3 volumes of a 20% solution of sodium sulphite, there is first precipitated the compound Cu_2SO_3, Cu_2C_2 of a clear red colour. When an excess of acetylene is employed, the dark red $Cu_2SO_3, 2Cu_2C_2$ is formed. When acetylene in excess acts for a long period on the well washed precipitates obtained from copper sulphate by means of sodium hydroxide or carbonate, or ammonium hydroxide, a black, explosive substance of the composition C_6Cu_3, H_2O is obtained.   G. D. L.

Action of Alkali Hydroxide and of Dry Silver Oxide on Trimethylene Bromide. B. F. FORTINSKI (*J. Russ. Phys. Chem. Soc.,* 1913, **45**, 568—580).—The author reviews the literature dealing with the formation of β-oxides, and describes attempts to prepare such an oxide from αγ-dibromopropane.

The action of aqueous potassium hydroxide on αγ-dibromopropane yields allyl alcohol and β-propylene glycol; the latter forms a *phenyl-urethane*, $C_{17}H_{18}O_4N_2$, m. p. 137—137·5°.

The reaction occurring between dry silver oxide and αγ-dibromo-propane is very energetic, but in presence of ether proceeds more smoothly, the products being β-propylene glycol and a compound of high boiling point which is converted into the same glycol by treatment with 10% sulphuric acid solution, and is hence probably a double β-oxide.   T. H. P.

Oxidation of Alcohols under the Influence of Heat. JEAN B. SENDERENS (*Compt. rend.,* 1913, **156**, 1909—1912).—As a pre-liminary to the investigation of the oxidation of alcohols in presence of various metals and metallic oxides, the action of hot air on various alcohols has been examined, and it is shown that oxidation occurs at lower temperatures than has previously been supposed.

The experiments were made by passing a mixture of dry air and the vapour of the alcohol into a vacuous glass tube, heated to the required temperature. The air was passed in at the rate of 100 c.c. per minute. Under these conditions, the oxidation of ethyl alcohol begins at 405°, and the issuing gas contains no oxygen, when the temperature is raised to 450°. The corresponding temperatures for *iso*butyl alcohol are 400° and 435°, and for *iso*amyl alcohol, 380° and 410°. The principal product is carbon monoxide, but some dioxide is also formed, and at the lower temperatures some aldehyde and acid are produced. In the case of ethyl alcohol the issuing gas contains also some ethylene, methane, and hydrogen. Magnesium turnings, finely-granulated zinc, aluminium powder, molybdic anhydride, blue tungstic oxide, thoria and silica only feebly assist or accelerate these reactions, whereas vanadic anhydride lowers the temperature at which oxidation begins, and accelerates the absorption of oxygen, and is therefore a true catalyst (compare Naumann, Moeser and Lindenbaum, A., 1907, ii, 273).
                                                            T. A. H.

The Hydrogenation of Some Secondary *d*-Ethylenic Alcohols in the Presence of Nickel. ROGER DOURIS (*Compt. rend.,* 1913, **157**, 55—57).—By the passage of secondary ethylenic alcohols of the type CHR:CHR'·OH over reduced nickel at 200°, they are converted, by isomerisation, into the corresponding ketones, $CH_2R·CH_2·COR'$, some of the saturated hydrocarbon $CH_2R·CH_2·CH_2R'$ being formed at the same time. The secondary ethylenic alcohols are readily obtained by the condensation of magnesium alkyl haloids with acraldehyde or crotonaldehyde (compare Grignard, A., 1901, i, 679). Thus *iso*amyl-propenylcarbinol is converted into *propyl isoamyl ketone*, $C_5H_{11}·COPr$, b. p. 177—179°, D_4^0 0·8362, D_4^{27} 0·8205, giving a *semicarbazone,* m. p. 107°. This ketone is also obtained by oxidation of *propylisoamyl-*

carbinol, $C_5H_{11}\cdot CHPr\cdot OH$, b. p. 184—186°/760 mm., D_4^0 0·8335, D_4^{16} 0·8199, prepared by the action of butaldehyde on magnesium *iso* amyl bromide.

*iso*Butylvinylcarbinol, when passed over reduced nickel at 200°, yields ethyl *iso*butyl ketone, b. p. 134—135°, giving an *oxime*, m. p. 129°. *cyclo*Hexylpropenylcarbinol yields cyclo*hexyl propyl ketone*, not yet obtained free from *butyl*cyclo*hexane*, b. p. 178—182°, D_4^0 0·8315 D_4^{20} 0·8178. The ketone gives a *semicarbazone*, m. p. 155°. W. G.

Action of Bromine on Ethyl Ether. ALEXANDER E. ARBUZOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 442—457).—In view of the divergent results obtained by McIntosh (T., 1905, **87**, 784; A., 1910, i, 808) and by Tschelinzev and Konovalov (A., 1909, i, 353; 1911, i, 415) the author has investigated the action of bromine on ethyl ether, with the following results.

At temperatures above 0°, this action yields no "oxonium dibromide," the sole product being Schutzenberger's perbromide (A., 1873, 487). If Tschelinzev's directions are followed closely, the same perbromide is obtained in an impure condition.

The value 9·13 Cal., given by Tschelinzev and Konovalov for the heat of formation of the dibromide, really represents the heat of formation of the perbromide, the value found by the author being 8·8 Cal. per gram-mol.

The interaction of ether and bromine in presence of solvents does not lend itself to calorimetric investigation, indefinite results being obtained.

At −80°, the action of bromine on ether yields the dibromide described by McIntosh (*loc. cit.*). T. H. P.

Vanadic Esters and Other Organic Vanadium Compounds WILHELM PRANDTL and LUDWIG HESS (*Zeitsch. anorg. Chem.*, 1913, **82**, 103—129).—The only previous preparation of vanadic esters is by Hall (T., 1887, **51**, 751). It is found that finely powdered vanadium pentoxide dissolves in many alcohols on boiling, and esters may be isolated from the solutions. Orthovanadic esters are readily prepared, with the exception of the methyl ester, and may be distilled without decomposition. Pyrovanadic esters have not been obtained. Meta-vanadic esters result from the action of small quantities of water on the ortho-esters, and form unstable solids, which decompose without melting. It is proposed to call the metavanadates, trivanadates. The further action of water gives the hexavanadates, which have not been obtained in a pure condition, as they are always mixed with trivanadates and colloidal vanadic acid.

The alcoholic solutions are of the colour of potassium dichromate when cold, but become lighter, and finally colourless, on heating, the colour change being completely reversible. This is due to the reaction in the case of the ethyl ester:

$$Et_4V_6O_{17} + 2Et\cdot OH \rightleftharpoons 2Et_2V_6O_9 + H_2O$$
<div style="text-align:center">Orange   Colourless.</div>
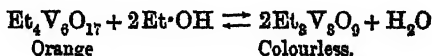
Any change tending to remove water should therefore cause a lightening of the colour. This is confirmed. The deeply coloured cold 1·5% solution of vanadium pentoxide in ethyl alcohol becomes colourless at 60—70°, but if diluted with an equal volume of absolute alcohol the change takes place at 50—60°, whilst the addition of a few drops of water raises the temperature of the change to above 70°. Anhydrous copper sulphate removes most of the colour at the ordinary temperature. An excess of alcohol in the cold does not alter the colour, but only affects the temperature at which the change takes place. The electrical conductivity diminishes at the same time as the colour, and only begins to increase with the temperature after decolorisation is complete. The conductivity also diminishes with increasing concentration of the alcohol. Pure ethyl orthovanadate has a very small conductivity. A solution of 1 mol. V_2O_5 in 1·09 mol. Na_2O exhibits similar colour changes to the ester.

The esters, especially *tert.*butyl orthovanadate, are very suitable for the preparation of clear colloidal solutions of vanadic acid, as the alcohol is easily removed by boiling.

Ethyl orthovanadate, Et_3VO_4, is a bright yellow liquid, b. p. 98·5°/16 mm., and 152°/145 mm., D^{15} 1·167, forming white crystals in liquid air. A greenish-black, crystalline *compound*, $V_4C_{16}H_{40}O_{18}$, is obtained by heating the ester at 160—170°, acetaldehyde and ether being evolved. Propyl orthovanadate, $Pr^a_3VO_4$, has b. p. 143°/24 mm., D^{15} 1·088, and forms an amber-coloured glass in liquid air. *n*-Butyl orthovanadate, $(C_4H_9)_3VO_4$, has b. p. 175°/22 mm., and the *iso*-propyl ester, b. p. 149°/16 mm., and D^{15} 1·033.

tert.Butyl orthovanadate, b. p. 117°/15 mm., forms colourless crystals, m. p. 45—47°. *iso*-Amyl orthovanadate forms yellow crystals, m. p. about 70°, b. p. 185—187°/18 mm. The tert.*amyl ester*, $(C_5H_{11})_3VO_4$, is a colourless liquid, b. p. 161°/19 mm., D^{17} 0·993, and is stable towards air and water.

Ethyl trivanadate (metavanadate), $Et_3V_3O_9$, is a light yellow powder, which readily decomposes. The molecular weight determination in phenol gives figures corresponding with the above formula. The n-*propyl* and iso-*amyl* esters have similar properties.

Vanadium oxychloride and sodium ethoxide react in benzene, forming *diethyl chloro-orthovanadate*, $VOCl(OEt)_2$, a dark red liquid, b. p. 103°/33 mm., D^{15} 1·366. By using suitable proportions, *ethyl dichloro-orthovanadate*, $VOCl_2\cdot OEt$, is obtained as a red liquid, b. p. 102°/49·5 mm.

The methyl esters have not been isolated, and glycerol and benzyl alcohol are oxidised by vanadium pentoxide.

Aniline hexavanadate, $(NH_3Ph)_4V_6O_{17},2H_2O$, forms reddish-brown, monoclinic prisms, $a:b:c = 0·4912:1:0·8511$, β 93°57'. Vanadium oxychloride forms an *additive product*, $VOCl_2,2Et_2O,2H_2O$.

<div align="right">C. H. D.</div>

The Methods for the Synthesis of Glycerides. Adolf Grün (*Ber.*, 1913, **46**, 2198—2200).—Polemical. A criticism of the results and conclusions of van Eldik Thieme (this vol., i, 701).   J. C. W.

The Preparation, Crystalline Structure, and Physical Properties of the Two Forms of Solid Nitroglycerin [Glyceryl Trinitrate]. HAROLD HIBBERT (*Eighth Inter. Cong. App. Chem.*, 1912, **4**, 37—57).—The statement of Kast (A., 1906, i, 922) as to the existence of two isomeric forms of glyceryl trinitrate, m. p. 2·8° and 13·5° respectively, has been considerably discounted by the failure of Nauckhoff (A., 1912, i, 63) to isolate the more fusible isomeride.

It is now found that if a mixture of wood pulp or powdered glass wool with glyceryl trinitrate (preferably a fresh specimen which has not been previously solidified) is cooled to − 40°, the latter crystallises in the new form described by Kast, for if glyceryl trinitrate at − 40° is inoculated with it the whole crystallises to a *labile* form, m. p. 2·0°. This labile isomeride passes readily into the stable form, m. p. 13·1°, for although when fused and cooled again to − 40° within one minute it spontaneously crystallises in the labile form, a longer period in the fused condition prevents any tendency to spontaneous crystallisation in any form. The solid labile form also passes rapidly into the stable one when inoculated with a trace of the latter or sometimes even on rubbing, the transformation being accompanied by a very appreciable development of heat ; the labile form also appears to be the more sensitive towards shock.

If the wood pulp used for the initial freezing contains powdered sodium nitrate, inoculation with this mixture causes more rapid crystallisation of glyceryl trinitrate, but in the more stable modification. Potassium nitrate has no such effect on the nature of the solid which separates, and it is possible that the separation of the less fusible isomeride is not due merely to the presence of the sodium nitrate, but depends on other conjoint factors of which the presence of moisture is one.

Microphotographs are given of the crystals of the two forms, of which the labile belongs to the triclinic and the stable to the rhombic system. Attention is drawn to the remarkable analogy between the isomeric forms of glyceryl trinitrate and those of benzophenone (Zincke, this Journ., 1871, **24**, 832 ; Auwers and Meyer, A., 1889, 611).

D. F. T.

Boiling Points of Solutions of Glyceryl Trinitrate. A. L. HYDE (*Eighth Inter. Cong. App. Chem*, 1912, **4**, 59—67).— Molecular-weight determinations have been effected by means of a modified form of the electrically heated Beckmann apparatus, with glyceryl trinitrate in various solvents ; as the concentrations attained in some cases over 75 grams of the nitrate to 100 of solvent, the results calculated from the usual law for dilute solutions can hardly be very trustworthy. With ether, methyl alcohol or chloroform as solvent, the results indicate an association which increases with the concentration, whilst with acetone the results are below the theoretical. Ethyl acetate gave, over a fairly wide range of concentrations, concordant results, which agreed well with the theoretical molecular weight and its application for such determinations should be useful, for example, in the estimation of diglycerol tetranitrate admixed with glyceryl trinitrate.

In a mathematical discussion of the results obtained with the three

solvents which give indications of association, it is shown that the rise in boiling point can be expressed by the equation $a = ch'$, where a is the rise in b. p., h the percentage composition of the solution, whilst c and n are constants.   D. F. T.

Separation of Glyceryl Trinitrate from Nitro-substitution Compounds. A. L. HYDE (*Eighth Inter. Cong. App. Chem.*, 1912, **4**, 69—76).—On shaking 1—3 grams of a mixture of glyceryl trinitrate and a nitro-derivative of toluene with 75 c.c. of carbon disulphide, four times with fresh portions (30 c.c.) of diluted acetic acid (65 acid : 35 water by volume), it is found that a fairly constant percentage of the nitrotoluene originally present in the mixture is left in the carbon disulphide, whilst the glyceryl nitrate is almost entirely to be found in the acetic acid. The quantity of nitrotoluene in the carbon disulphide is determined by careful evaporation after first washing the solution with water.

The following nitro-compounds were tried : *o*- and *p*-nitrotoluenes, liquid dinitrotoluene and its isomerides, m. p. 48° and 68° respectively, also liquid trinitrotoluene. Knowing the proportion of each of these to be found in the carbon disulphide after the above procedure, it is possible to apply this process to the rough estimation of any one of these nitro-compounds in a binary mixture with glyceryl trinitrate.
                                                              D. F. T.

Phytic Acid in Cottonseed Meal and Wheat Bran. J. B. RATHER (*J. Amer. Chem. Soc.*, 1913, **35**, 890—895).—The Patten and Hart modification of Posternak's method for the separation of inositolphosphoric acid, or so-called phytic acid, from wheat bran gives a product containing at least 5% of inorganic impurity mainly iron and aluminium phosphates, so that the formula $C_2H_8O_9P_2$ based on such results is probably erroneous (compare Posternak, A., 1903, ii, 679). Examination of the phosphorus compounds of wheat bran which are soluble in 0·2% hydrochloric acid and of cottonseed meal which are soluble in similar acid and also extracted by subsequent treatment with 0·2% ammonium hydroxide, indicates that by purification they yield an identical acid $C_{12}H_{41}O_{42}P_9$; this on heating with sulphuric acid undergoes scission into inositol and phosphoric acid and it is free from pentosans.   D. F. T.

Trimethylene Trisulphide and Its Oxidation Products. OSCAR HINSBERG (*J. pr. Chem.*, 1913, [ii], **88**, 49—58. Compare A., 1912, i, 546).—Trimethylene trisulphoxide dissolves in concentrated hydrochloric acid, yielding a compound which is resolved into its components on the addition of alcohol, and is considered to be a basic salt containing the group $CH_2 \cdot SCl \cdot OH$; when kept the solution deposits a colourless oil. In view of these results, the author is undertaking a study of the action of the halogen acids on the trisulphoxide, the present paper dealing particularly with the action of hydriodic acid.

Trimethylene trisulphoxide dissolves in warm dilute hydriodic acid and crystallises out again unchanged. When dissolved in concentrated

hydriodic acid (1 gram in 20—25 c.c., D = 1·96) and the solution maintained for twenty-four hours at the ordinary temperature, the trisulphoxide is reduced to a new labile (β) *trimethylene trisulphide*, which is obtained as yellow, crystalline precipitate on diluting the solution with water. The new trisulphide has m. p. 247° (decomp.), and passes into the stable (α) trisulphide of m. p. 216° on crystallisation from chloroform, acetic acid, benzene or alcohol. Attempts to effect the reverse transformation by the action of acetyl chloride, ethyl iodide or iodine proved successful.

The β-trisulphide may also be prepared by dissolving the α-compound in concentrated hydriodic acid, and maintaining the solution for several days at the ordinary temperature.

A solution of trimethylene trisulphoxide in seven times its weight of hydriodic acid (D 1·96) deposits after twelve hours stout, brown plates or prisms of *β-trimethylene trisulphide tri-iodide*, $CH_2 \underset{SI \cdot CH_2}{\overset{SI \cdot CH_2}{<}} > SI$, which melts indefinitely at 118—123° (decomp.), and loses its iodine completely when exposed to the air for eight days, or when heated at 60°, yielding β-trimethylene trisulphide. If the tri-iodide is crystallised from chloroform and then heated at 60° until the iodine is removed, either the pure α-trisulphide or a mixture of the α- and β- forms is obtained.

The tri-iodide combines with iodine in chloroform solution, yielding a *tetraiodide*, $C_3H_6S_3I_4$, which is derived from the α-trisulphide, and crystallises in elongated prisms, resembling iodine, m. p. 100° (decomp.), with previous sintering. The tetraiodide is more stable than the tri-iodide, but loses its iodine completely when heated for several hours at 60°, or when exposed to the air for several weeks yielding α-trimethylene trisulphide. If kept for several weeks in contact with aqueous sodium hydrogen carbonate, the tetraiodide loses only part of the iodine, with the formation of a brown substance which is probably the tri-iodide of α-trimethylene trisulphide.

The author has also investigated the action of hydrogen peroxide on the isomeric trisulphides, in the hope of obtaining the corresponding trisulphoxides, but no evidence of the existence of such isomerides was obtained.

When heated for two hours with 10—15% hydrogen peroxide on the water-bath, the trisulphides are converted into trimethylene trisulphoxide, which is accompanied by *trimethylenedisulphonesulphoxide*, $CH_2 \underset{SO_2 \cdot CH_2}{\overset{SO_2 \cdot CH_2}{<}} > SO$.

The latter compound is separated from the trisulphoxide by taking advantage of its sparing solubility in water and organic solvents. It crystallises in colourless needles, which become brown at 270° without melting.

The action of hydrogen peroxide on the trisulphide also leads to the formation of *trimethylenedisulphoxidesulphide*, $CH_2 \underset{SO \cdot CH_2}{\overset{SO \cdot CH_2}{<}} > S$, which is readily soluble in water and crystallises in slender, colourless needles; m. p. about 210° (decomp.).

With respect to the isomerism of the trimethylene trisulphides, it is

pointed out that the existence of the two forms cannot be explained by a *cis-trans*-isomerism as in the case of the trithiobenzaldehydes, for, owing to the symmetrical structure of the molecule, stereo-isomerism of this kind is excluded. The author inclines to the view that the isomerism is of a new type determined by spatial configuration of the sulphur atom, and suggests that the two modifications of tri-thiobenzaldehyde and of other substituted trithioformaldehydes may be sulphur isomerides of this type and not *cis-trans*-isomerides is usually imagined.   F. B.

Uranyl Formate. Reply to Courtois. WILLIAM ŒCHSNER DE CONINCK and ALBERT RAYNAUD (*Bull. Soc. chim.*, 1913, [iv], 13, 665—666. Compare this vol., i, 333).—A reply to Courtois (this vol., i, 585), in which the authors suggest that the salts used were different and that the experiments were conducted under different conditions.
                                                         W. G.

The Mechanism of the Hell-Volhard Reaction. II. OSSIAN ASCHAN [With (Frl.) ELLA EUROPAEUS] (*Ber.*, 1913, 46, 2162—2171. Compare A., 1912, i, 599).—Meyer (A., 1912, i, 941) expressed the opinion that the formation of a mixture of α-bromo-acid chloride and α-bromo-acid bromide by the action of bromine on acid chlorides is due, in the first place, to direct α-substitution, followed by a reaction between the liberated hydrogen bromide and the bromo-acid chloride, as in the equation : $CH_2Br\cdot COCl + HBr = CH_2Br\cdot COBr + HCl$.

The author now shows that anhydrous sulphuric acid does not react with acetyl chloride in the cold, and also describes the action of hydrogen chloride and bromide on the acid haloids. He finds that hydrogen bromide will convert acetyl chloride into acetyl bromide (compare Staudinger and Anthes, this vol., i, 616), but that, con-versely, hydrogen chloride will transform acetyl bromide into acetyl chloride. Such changes cannot both be due to direct substitution, but are best explained by assuming the formation of the intermediate compound, $CH_3\cdot C{<}^{Br}_{Cl}{-}OH$, which can part with either hydrogen chloride or bromide, according to the conditions. Thus, whether it is assumed that direct α-substitution is the first step in the action of bromine on acid chlorides, or that enolisation of the carboxyl group takes place, the formation of the same intermediate product must be assumed.

1. $CH_3\cdot COCl + Br_2 = CH_2Br\cdot COCl + HBr = CH_2Br\cdot C{<}^{Br}_{Cl}{-}OH.$

2. $CH_3\cdot COCl {\rightarrow} CH_3\cdot C(OH)Cl + Br_2 = CH_2Br\cdot C{<}^{Br}_{Cl}{-}OH.$
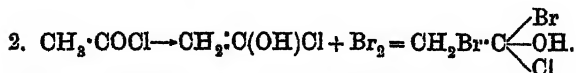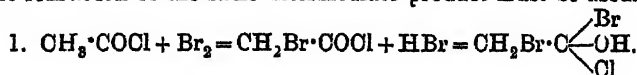
The following cases have been studied, and the amount of transforma-tion that takes place during definite intervals of time, calculated from halogen estimations which were controlled by density determinations : the action of hydrogen bromide on acetyl chloride, chloroacetyl chloride and bromoacetyl chloride, and the action of hydrogen chloride on acetyl bromide, chloroacetyl bromide and bromoacetyl bromide.   J. C. W.

Trichloroacrylic Acid and Certain of its Derivatives.
JACOB BOESEKEN and P. DUJARDIN (*Rec. trav. chim.*, 1913, 32, 97—111).—Heptachloropropane, b. p. 115°/12 mm., obtained according to Prins' method (A., 1911, i, 173) by the action of chloroform on pentachloroethane in the presence of aluminium chloride, is converted by alcoholic potassium hydroxide into hexachloropropylene, b. p. 209—210°/760 mm., 99°/15 mm. (compare Fritsch, A., 1898, i, 63). The latter is conveniently converted into trichloroacrylic acid, m. p. 76°, by the action of slightly diluted sulphuric acid at 135° or by a boiling aqueous suspension of barium carbonate. The *sodium*, *potassium*, and *magnesium* salts of this acid are readily soluble, whilst the *lead* salt crystallises in leaflets sparingly soluble in water. From measurement of the conductivity, the acid appears to be dissociated to about the same extent as oxalic acid, whilst it has approximately the same influence on the rate of inversion of sucrose as hydrochloric acid in $\frac{1}{5}N$-solution.

Trichloroacrylyl chloride, prepared by the action of an excess of thionyl chloride on the acid, has b. p. 158°/760 mm., n_D^{15} 1·52709, and when treated with ammonia in benzene solution is converted into the corresponding amide, m. p. 96° (compare Fritsch, *loc. cit.*). The latter is transformed by phosphoric oxide into trichloroacrylonitrile,
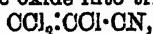
$$CCl_2{:}CCl{\cdot}CN,$$

m. p. 20°, n_D^{20} 1·5100.

A series of mixed aromatic ketones of the general formula
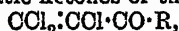
$$CCl_2{:}CCl{\cdot}CO{\cdot}R,$$

has been prepared either by gradual addition of the benzenoid derivatives to the stable molecular compound, $CCl_2{:}CCl{\cdot}COCl{\cdot}AlCl_3$ (compare Böseken and Hasselbach, this vol., i, 335), or by addition of the acid chloride to a mixture of benzenoid derivative and catalyst, reaction being continued only until one molecule of hydrogen chloride had been evolved. In this manner, the following ketones have been obtained : (i) *phenyl trichlorovinyl ketone*, b. p. 138°/2 mm., D_4^{15} 1·3902, n_D^{27} 1·5798, which unites with chlorine in sunlight to form pentachloropropiophenone, m. p. 82·5° (compare Böseken and Hasselbach, *loc. cit.*); (ii) *p-chlorophenyl trichlorovinyl ketone*, $C_6H_4Cl{\cdot}CO{\cdot}CCl{:}CCl_2$, b. p. 159°/17 mm., m. p. 19°, from trichloroacrylyl chloride and chlorobenzene. The isomeric *o* chloro derivative could not be isolated from the product. When acted on by chlorine in sunlight, *p*-chlorophenyl trichlorovinyl ketone yields p-*chlorophenyl pentachloroethyl ketone*, white crystals, m. p. 116°; (iii) p-*tolyl trichlorovinyl ketone*, $C_6H_4Me{\cdot}CO{\cdot}CCl{:}CCl_2$, b. p. 147·5°/10 mm., (iv) m-*xylyl trichlorovinyl ketone*, b. p. 165°/14 mm.; (v) p-*xylyl trichlorovinyl ketone*, b. p. 161°/13 mm.; (vi) sec.-*propylphenyl trichlorovinyl ketone*,

$$CHMe_2{\cdot}C_6H_4{\cdot}CO{\cdot}CCl{:}CCl_2,$$
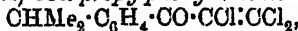
b. p. 173°/12 mm. In the three latter cases, reaction is very vigorous, but seems also to proceed in another direction, since evolution of hydrogen chloride continues after the quantity corresponding to one molecule has been evolved. (vii) ψ-*Cumyl trichlorovinyl ketone*, $C_6H_2Me_3{\cdot}CO{\cdot}CCl{:}CCl_2$, m. p. 57°. (viii) p-*Anisyl trichlorovinyl ketone*, m. p. 26·5°. In this case, the action is far less rapid than with toluene. Reaction was carried out in carbon disulphide solution when

a certain amount of the ketone was simultaneously decomposed with formation of *p*-hydroxybenzoic acid. (ix) *Phenetyl trichlorovinyl ketone*, m. p. 58°, D_4^5 1·3202, n_D^{18} 1·5726.

The position of the sub-tituents in the above ketones is deduced from a study of their decomposition by alkali. When mixed with potassium alkoxides they are immediately decomposed with separation of the potassium salt of the aromatic acid according to the equation : $X \cdot C_6H_4 \cdot CO \cdot CCl \colon CCl_2 + KOH = X \cdot C_6H_4 \cdot CO_2K + HCCl \colon CCl_2$. In this manner, benzoic, *p*-toluic, anisic, *p*-ethoxybenzoic, and *p*-chlorobenzoic acids were obtained from phenyl trichlorovinyl ketone, *p*-tolyl trichlorovinyl ketone, *p*-anisyl trichlorovinyl ketone, *p*-phenetyl trichlorovinyl ketone, and *p*-chlorophenyl trichlorovinyl ketone respectively.

H. W.

Methylation of Aliphatic Compounds by means of Methyl Sulphate. EUGÈNE GRANDMOUGIN, EM. HAVAS and G. GUYOT (*Chem. Zeit.*, 1913, **37**, 812—813).—Although methyl sulphate has been extensively used in the methylation of aromatic substances, very few instances have been recorded of its use with aliphatic compounds. The authors have therefore investigated its applicability to the latter class and find that, in a series of typical methylations, this reagent can advantageously replace the customary methyl iodide under definite conditions of experiment.

Ethyl methylacetoacetate is obtained in 85% yield by the gradual addition of methyl sulphate to a solution of ethyl sodioacetoacetate in methyl alcohol under definite conditions of temperature which are fully described in the original, and, when again methylated under similar conditions, gives an 87% yield of ethyl dimethylacetoacetate.

In an analogous manner, ethyl methylmalonate and ethyl dimethylmalonate may be prepared, the yield of the former being 80—85%. The latter substance can also be obtained directly from ethyl malonate, the most favourable proportions being ester (1 mol.), sodium (3 atoms) and methyl sulphate (3 mols.). Employment of the theoretical quantities leads to the formation of a mixture of mono-methyl- and dimethyl-malonic esters.

Phenylmethylpyrazolone can also be readily methylated by means of methyl sulphate. When methyl sulphate is slowly added to a solution of sodium methoxide and phenylmethylpyrazolone in methyl alcohol,

5-methoxy-1-phenyl-3-methylpyrazole, $\begin{smallmatrix} N\text{---}NPh \\ CMe \cdot CH \end{smallmatrix} \!\!>\! C \cdot OMe$, is obtained

(compare Knorr, A., 1895, i, 397 ; von Pechmann, A., 1895, i, 494). When, on the other hand, methylation is accomplished by the addition of methyl sulphate to a boiling solution of sodium hydroxide in the minimum quantity of water and methylphenylpyrazolone in methyl alcohol, antipyrine is obtained in 80% yield.

The conversion of aminoantipyrine into pyramidone can also be readily effected by means of methyl sulphate.   H. W.

Aliphatic Nitrosocarboxylic Esters. JULIUS SCHMIDT and EMIL AECKERLE (*Annalen*, 1913, **398**, 251—256).—*Ethyl chloromethyl-acetoacetate*, $CH_3 \cdot CO \cdot CMeCl \cdot CO_2Et$, b. p. 116—117°/75 mm, D_4^{18} 1·157,

n_D^{15} 1·4382, obtained from ethyl methylacetoacetate and sulphuryl chloride, is not attacked by nitrous fumes at 0°. Ethyl a-benzoyl-propionate is converted by careful treatment with nitrous fumes at 0° into *ethyl a-nitroso-a-benzoylpropionate*, $C_6H_5 \cdot CO \cdot CMe(NO) \cdot CO_2Et$, a dark blue liquid, n_D^{19} 1·4902, which exhibits oxidising properties, and gradually decomposes into benzoic acid and ethyl a-nitrosopropionate.

These two experiments indicate that the formation of nitrosocarboxylic esters by the action of nitrous fumes on the esters of alkylated ketonic acids is represented by the scheme:

$$R \cdot CO \cdot CHR' \cdot CO_2Et \longrightarrow R \cdot CO \cdot CR'(NO) \cdot CO_2Et \xrightarrow{H_2O}$$
$$R \cdot CO_2H + NO \cdot CHR' \cdot CO_2Et. \quad C. S.$$
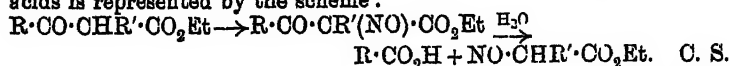
Ricinstearolic Acid. GEORG MÜHLE (*Ber.*, 1913, **46**, 2091—2098).— The presence of the triple linking in ricinstearolic acid is confirmed by the addition of iodine which occurs when the acid is treated with the calculated quantity of iodine and a trace of dried ferrous iodide in carbon disulphide or warmed with an acetic acid solution of iodine, the temperature being kept, however, below 40°; the resultant *ricinstearolic acid di-iodide*, $CH_3Me \cdot [CH_2]_4 \cdot CH(OH) \cdot CH_2 \cdot CI:CI \cdot [CH_2]_7 \cdot CO_2H$, forms colourless needles, m. p. 62°, decomp. at 175°; *sodium* and *barium* salts, colourless needles; *mercury* salt, yellow powder; *methyl* ester, pale yellow oil, decomp. at 150°.

Recinstearolic acid, needles, m. p. 51°, b. p. 260°/10 mm. without decomposition, obtained by successive treatment of castor oil with bromine and potassium hydroxide solution, is accompanied by a small quantity of *θιλ-trihydroxystearic acid*, m. p. 110—111°,

$$CH_3Me \cdot [CH_2]_4 \cdot CH(OH) \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot [CH_2]_7 \cdot CO_2H,$$

identical with the *a-isotrihydroxystearic* acid obtained earlier by oxidation of castor oil. A specimen of ricinstearolic acid kept for twenty years without any precautions for the exclusion of atmospheric moisture gave a deposit of a *dihydroxystearic acid*, leaflets, m. p. 140—141°. The author was unable to reproduce the results of earlier workers, who state that on distillation of ricinelaidic acid and of ricinoleic acid under reduced pressure, an acid, $C_{18}H_{32}O_2$, is produced.

Acetylricinelaidic acid, obtained by acetylation of ricinelaidic acid with acetic anhydride, is a bright yellow, viscid oil; *acetylricinstearolic acid* is very similar.

Methyl ricinstearolate, obtained by esterification with a methyl alcoholic solution of hydrogen chloride, or in alkaline solution with methyl sulphate, is a colourless oil, b. p. 225°/12 mm., D 0·9389; *ethyl* ester, b. p. 230°/12 mm., D 0·9371.

Glyceryl monoricinstearolate, obtained from a-monochlorohydrin and dried sodium ricinstearolate at 150°, is a pale yellow, viscid oil; *glyceryl triricinstearolate*, from trichlorohydrin and sodium ricinstearolate at 190—200° under pressure, is of similar appearance.

The action of phosphorus pentachloride on ricinstearolic acid in the cold, yields a chlorostearolic acid, $C_{18}H_{31}O_2Cl$, a pale yellow, viscid oil, which cannot be distilled without decomposition. D. F. T.

Thorium Chloro-oxalate. A. COLANI (*Compt. rend.*, 1913, **156**, 1907—1909. Compare A., 1913, i, 444; Hauser and Wirth, A., 1912, i, 827).—Hauser and Wirth's method is the most convenient for

the preparation of this salt, which has the composition assigned to it by Wyrouboff and Verneuil (A., 1899, ii, 598; compare Kohlschütter, A., 1902, i, 11). The behaviour of thorium oxalate with hydrochloric acid of various strengths at various temperatures is shown by lists of analytical results in the original. The chloro-oxalate loses from 0·5 to 1·00% of thorium by volatilisation of the chloride when heated rapidly, but no loss takes place when heat is gradually applied and the thoria, produced under the latter conditions, contains only 0·1 to 0·2% of chlorine. Similarly, thorium oxalate precipitated in solutions of moderately concentrated hydrochloric acid contains very little chlorine. In these two respects, thorium behaves differently from the rare earths   Determinations of the solubility of thorium chloro oxalate in hydrochloric acid are given in the original, and show that the solubility is much diminished in presence of oxalic acid, but that in the absence of the latter and with liquids containing 21·2% or less of hydrogen chloride, decomposition is rapid and complete into oxalate and chloride.   T. A. H.

Barium Malonate Jellies and their Micro structure. FRIEDRICH FLADE (*Zeitsch. anorg. Chem.*, 1913, **82**, 173—191).—The transformation of barium malonate jellies into powders takes place more slowly than with other barium salts (compare Neuberg and Neimann, A., 1906, ii, 753; Neuberg and Rewald, A., 1908, ii 39).

Equivalent quantities of solutions of malonic acid and barium hydroxide in methyl alcohol and glycerol are freed from air-bubbles by placing under an exhausted bell-jar and mixed. The greater the proportion of glycerol, the slower the formation of the jelly. If the glycerol is removed by means of methyl alcohol, it may be replaced by other liquids, such as chloroform or benzene, without destruction of the jelly, and with a great increase in its transparency. Much of the liquid may be removed by pressure between filter-paper, or by evaporation. The residue is barium malonate with $2H_2O$. Warming does does not liquefy the jelly.

Microscopical observations show that the jelly is made up of a network of fibres of barium malonate, in which the liquid is held as in a sponge. These fibres are stained deeply by methyl violet. The fibres are about 0 5 mm. long and 0 0001—0·0003 mm. thick, and are shown to be crystalline by their behaviour in polarised light.   C. H. D.

Stereochemistry of the Halogen Substituted Succinic Acids. BROR HOLMBERG (*J. pr. Chem.*, 1913, [ii], **87**, 456—479).—The author has shown previously (A., 1912, i, 603) that during the hydrolysis of the sodium salt of *l*-bromosuccinic acid, the elimination of bromine proceeds at a greater rate than the increase in the acidity of the solution, and from these results has drawn the conclusion that the formation of malic acid from the bromo-acid is preceded by the formation of propiolactonecarboxylic acid.

The present paper deals with conditions favourable to the formation of the lactone and also with the hydrolysis of the sodium salts of *l*-chlorosuccinic, *l*-iodosuccinic and *l*-bromosuccinamic acids. In the case of bromosuccinic acid, the addition of neutral salts of weak acids

(formate, acetate, succinate and malate) increases the velocity of bromine ion formation, but diminishes the rate of hydrolysis of the lactone. Further, the formation of the lactone proceeds less readily with chlorosuccinic and bromosuccinamic acid than with bromosuccinic acid.

It is also found that the hydrolysis of the lactone yields either a *l*- or *d*-malic acid accordingly as it is carried out in acid or alkaline solution. Thus, a solution of *l*-bromosuccinic acid after being exactly neutralised with sodium hydroxide was maintained for twenty-four days at 25°, and then contained 10% of unchanged bromo-acid, 25% of lactone and 65% of malic and fumaric acids; after the bromo-acid and lactone had been completely hydrolysed by heating the solution on the water-bath, the malic acid obtained from the product was lævorotatory. On the other hand, when the hydrolysis was effected by excess of sodium hydroxide, the resulting malic acid contained a preponderance of the dextrorotatory form.

Similar results were obtained in the case of silver oxide; the action of excess of the oxide on *l*-bromosuccinic acid yields a dextrorotatory malic acid, whilst the theoretical amount necessary to form the neutral silver salt gives rise to a lævorotatory acid. F. B.

Symmetric and Asymmetric Acid Dichlorides. II. ERWIN OTT (*Ber.*, 1913, **46**, 2172—2175. Compare A., 1912, i, 828).—A further difference in reactivity between symmetric and asymmetric chlorides is in their behaviour on treatment with hydrogen and platinum black. Whereas fumaryl and chlorofumaryl chlorides immediately "poison" the catalyst so that not even limonene can be reduced in their presence, chloromaleyl chloride may easily be reduced to *n*-butyric acid. The hydrogen chloride which is formed gradually impedes the reduction, but if it is removed from time to time by evacuation, the absorption of hydrogen can be carried almost to the theoretical value. The reduction of dibromomaleyl chloride, however, could only be carried to one-fifth before "poisoning" of the platinum took place, whilst *as-o*-phthalyl chloride and phthalyl tetrachloride could not be reduced at all. J. C. W.

Ethyl Cyanotartronate and its Reactions with Amines. RICHARD SYDNEY CURTISS and LLOYD F. NICKELL (*J. Amer. Chem. Soc.*, 1913, **35**, 885—890. Compare Curtiss and others, A., 1911, i, 353, 366; A., 1909, i, 763).—The reaction between anhydrous hydrogen. cyanide and ethyl oxomalonate is greatly influenced by small variations in temperature; at 30° it is complete in twenty-four hours, the product being *ethyl cyanotartronate*, $OH \cdot C(CN)(CO_2Et)_2$, an undistillable oily liquid, D_{20}^{10} 1·16; it is soluble in alkaline solutions to a yellow solution, and if treated in ether with sodium, deliquescent, colourless crystals of an unstable *substance* slowly separate.

Ethyl cyanotartronate in cooled ethereal solution reacts with many amines, producing compounds which in all probability have an amidine structure; thus dipropylamine yields a crystalline *substance*,

$$NPr_2 \cdot C(:NH) \cdot C(CO_2Et)_2 \cdot OH,$$
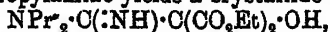
m. p. 72·5—73°. With diethylamine an analogous *compound*, m. p. 56°, was obtained, whilst benzylamine gave in a similar manner a

substance, m. p. 55—56°. These three substances on exposure to the atmosphere or when kept at 25°, undergo decomposition with formation of a tarry mass. Ethylamine, *iso*butylamine and benzylethylamine gave rise to uncrystallisable syrups, triethylamine slowly produced a red, tarry mass, whilst ammonia formed a very unstable, crystalline *substance*. With aromatic amines there was apparently no reaction.

<div align="right">D. F. T.</div>

Catalytic Decomposition of Aldehydes. M. I. Kuznecov (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 557—568).—In his earlier experiments on the oxidation of methyl alcohol by means of atmospheric oxygen with a view to preparing formaldehyde, the author found that the aldehyde was always accompanied by carbon monoxide and hydrogen in proportions depending on the temperature conditions and on the nature of the catalyst employed (*Bull. Charkov Technol. Inst.*, 1909). These two products result from the decomposition of aldehyde previously formed: $CH_2O = CO + H_2$.

Further experiments show that resolution of the aldehydic group with formation of carbon monoxide is a general reaction for all aldehydes.

The first series comprises measurements of the degree of decomposition of formaldehyde at various temperatures and under the influence of a number of different metals and of wood charcoal, asbestos and powdered Jena glass. The results show that the action depends not only on the chemical character of the catalyst but also on its physical condition. For instance, with copper turnings at 500° there is no decomposition, and at 600° only 4% of the aldehyde is attacked; with copper reduced from the oxide by the action of hydrogen, 9·2% of the aldehyde is decomposed at 500°; and with copper obtained by reduction of copper sulphate solution by means of alkaline formaldehyde, the action proceeds to the extent of 35·3, 84·2, 94·8 and 95·8% at 200°, 300°, 400° and 500° respectively. With different forms of other metals smaller variations are observed.

In the second series the products obtained by the decomposition of the following aldehydes by palladium black were investigated: formaldehyde, acetaldehyde, paracetaldehyde, propaldehyde, *n*-butaldehyde, *iso*butaldehyde, benzaldehyde and *p*-tolualdehyde. The results show that the aldehyde group is decomposed by palladium into carbon monoxide and hydrogen, the latter combining with the hydrocarbon radicle: $R \cdot CHO = RH + CO$. In the cases of propaldehyde and the butaldehydes, free hydrogen and unsaturated hydrocarbons are also obtained owing to the partial decomposition of the saturated hydrocarbons originally formed. T. H. P.

Stability of Paracetaldehyde. R. Richter (*Pharm. Zeit.*, 1913, **58**, 482—483).—A series of experiments has been performed on the stability of paracetaldehyde alone, in aqueous solution and in the presence of various pharmaceutical preparations. The author is led to the following conclusions: (1) pure paracetaldehyde, free from acid and acetaldehyde, can be kept for sixteen months without alteration; the presence of these substances even in small quantity,

however, induces a gradual decomposition of the paracetaldehyde; (2) in the presence of pure raspberry juice without addition of water, paraldehyde remains unchanged during two months; (3) when mixed with water and a syrup composed of sugar and citric acid, paracetaldehyde speedily undergoes conversion into acetaldehyde; after two months, 7·8% of the paracetaldehyde had undergone such conversion; (4) in aqueous solution, without addition of juice, formation of acetaldehyde occurs slowly but continuously. H. W.

Catalytic Actions. VII. Polymerisation of Chloral. JACOB BOESEKEN and A. SCHIMMEL (*Rec. trav. chim.*, 1913, **32**, 112—127).— The authors have studied the polymerisation of chloral in the presence of pyridine. For this purpose, known weights of dry chloral and pyridine have been preserved for a month at the ordinary temperature, at the end of which time a quasi-stable state had been reached. The contents of the flask were then treated with a large quantity of dilute hydrochloric acid, which combined with the pyridine and dissolved unchanged chloral. The metachloral which is insoluble in this reagent was estimated by decomposition with potassium hydroxide.

As the quantity of pyridine employed relatively to the amount of chloral increases, the latter becomes more completely transformed into metachloral, until, in the presence of about $\frac{1}{5}$ mol. pyridine, transformation is practically quantitative. Beyond this point, the amount of metachloral formed diminishes with increasing quantities of pyridine. The separation of metachloral is incomplete, whatever the quantity of catalyst employed. From determinations of the vapour tension of metachloral, obtained from chloral either by means of pyridine or fuming sulphuric acid, it appears that the true equilibrium of the system, chloral $\rightleftarrows$ metachloral, is situate practically entirely on the side of metachloral, and thus, that starting from chloral, this equilibrium is not obtained after a month even in the presence of considerable quantities of catalyst. This result is probably due to the absorption of pyridine by the polymeride which separates in the colloidal state.

When pyridine (4—5 mols.) is added to chloral (100 mols.) a rapid separation of a gelatinous mass occurs. After several weeks, a second change is observable in that the metachloral in contact with the walls of the vessel again becomes transparent, forming a membrane greatly resembling a collodion pellicle. This *transparent metachloral* does not appear to retain pyridine and has a vapour tension below that of the equilibrium mixture.

When pure metachloral is placed in an atmosphere of pyridine, it almost immediately becomes opaque, and then has the same vapour tension as the pseudo-binary system. Subsequently, it becomes gelatinous and then completely liquid.

In the presence of larger quantities of catalyst, less chloral is transformed into the polymeride, although equilibrium is more certain to be obtained in this case since a portion of the metachloral dissolves in the pyridine. The catalyst here exerts a marked influence on the

equilibrium, although it has not been found possible to isolate an additive compound of pyridine and chloral.

The phenomena here observed are analogous to those encountered in the polymerisation of chloral by means of fuming sulphuric acid (Boeseken, *Rec. trav. chim.*, 1910, **29**, 104) or aluminium chloride.

<div align="right">H. W.</div>

Modifications of Metachloral and Decomposition of Chloral by Aluminium Chloride. Perchlorobutanal, $CCl_3 \cdot CCl_2 \cdot CCl_2 \cdot CHO$. JACOB BOESEKEN and A. SCHIMMEL (*Rec. trav. chim.*, 1913, **32**, 128—133).—Metachloral is known in a gelatinous modification immediately obtained by the addition of pyridine to anhydrous chloral, an opaque modification formed by the action of different catalysts on chloral, and representing the equilibrium mixture of the system chloral⇌metachloral and as a transparent modification which is slowly produced when pyridine remains in contact with chloral. The latter is probably the only pure metachloral, the others being mixtures of it with unchanged chloral and catalyst. Attempts have been made to obtain the polymeride of chloral described by Combes (A., 1887, 127) as the product of the action of aluminium chloride on chloral. The authors have repeated his experiments, and have also somewhat modified the conditions, and find that the products are tetrachloroethylene, pentachloroethane and relatively very small amounts of perchlorobutanal, b. p. 145·5—147°/20—26 mm., m. p. 46·5—48°, molecular weight in benzene solution, 334. The latter is quantitatively decomposed by alkali according to the equation :

$$CCl_3 \cdot CCl_2 \cdot CCl_2 \cdot CHO + 2KOH = C_3Cl_6 + KCl + HCO_2K + H_2O.$$
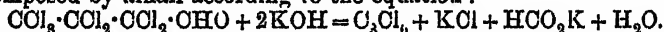
When heated with excess of aluminium chloride, it is decomposed with evolution of carbon monoxide.

<div align="right">H. W.</div>

The Catalytic Preparation of Ketones. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1913, [iv], **13**, 666—671).—A reply to Senderens (A., 1911, i, 134, 302 ; this vol., i, 342) in which the author maintains the utility of his method using zinc oxide, and more especially cadmium oxide, as a catalyst in the preparation of ketones from acids.

<div align="right">W. G.</div>

Cerium Acetylacetonates. ANDRÉ JOB and PAUL GOISSEDET (*Compt. rend.*, 1913, **157**, 50—52).—Urbain (compare A., 1897, i, 236) prepared a basic cerous acetylacetonate by the action of cerous hydroxide on acetylacetone, and Biltz (compare A., 1904, i, 715) obtained the crystalline, neutral cerous salt by the action of cerous nitrate on an ammoniacal solution of ammonium acetylacetonate. Adopting Urbain's method the author has now prepared the ceric compound in a crystalline state. An excess of acetylacetone is added to a suspension of ceric hydroxide in water and the mixture agitated, when it slowly turns brown, and at the end of several days deep red needles of *ceric acetylacetonate* separate, having the composition $Ce(CHAc_2)_4,11H_2O$. On drying this salt in a vacuum and crystallising it from carbon tetrachloride, it is obtained in the anhydrous state as black crystals, m. p. 171—172°, having a metallic lustre. It is slightly soluble in water, and in solution is readily hydrolysed except

in the presence of excess of acetylacetone. The anhydrous salt is soluble in most organic solvents to a deep red solution, the colour rapidly disappearing in sunlight in the case of oxidisable solvents.

W. G.

Syntheses by means of Sodamide. II. Alkylation of Aliphatic Ketones. ALBIN HALLER and EDOUARD BAUER (*Ann. Chim. Phys.*, 1913, [viii], **29**, 313—349).—The authors' work (A., 1909, i, 108) on the alkylation of acetophenone and analogous substances by the successive action of sodamide and alkyl haloids has been extended to aliphatic ketones.

When an ethereal solution of pinacoline is treated successively with sodamide (1 mol.) and methyl iodide (1·1 mol.), a mixture of unchanged material, methyl- and dimethyl-pinacoline is obtained from which $\beta\beta$-dimethylpentan-γ-one, $CMe_3 \cdot CO \cdot CH_2 \cdot CH_3$, b. p. 124—126°, can be isolated by repeated fractional distillation. This substance has already been described by Wischnegradsky (A., 1875, 878). The *oxime* has m. p. 79—80°. When the methylation is repeated until no further action occurs in ethereal solution, $\beta\beta\delta$-trimethylpentan-γ-one, $CMe_3 \cdot CO \cdot CHMe_2$, b. p. 133—135° (compare Nef, A., 1900, i, 349), is obtained. It has D_4^0 0·80536, n_α^{27} 1·40304, n_D^0 1·40513, n_β^{27} 1·41020, n_γ^{10} 1·41429. The oxime has m. p. 141°. When reduced by sodium and alcohol, the ketone yields $\beta\beta\delta$-*trimethylpentan-γ-ol*,

$$CMe_3 \cdot CH(OH) \cdot CHMe_2,$$

b. p. 145—148°, the *phenylurethane* of which has m. p. 79°. $\beta\beta\delta$-Trimethylpentan-γ-one can be further methylated by means of sodamide and methyl iodide in benzene solution, when $\beta\beta\delta\delta$-*tetramethylpentan-γ-one*, $CMe_3 \cdot CO \cdot CMe_3$, is obtained. It has b. p. 150—151°, D_1^{20} 0·81992, n_α^{23} 1·41485, n_D^{25} 1·41702, n_β^{10} 1·42224, n_γ^{27} 1·42643. It does not appear to form an oxime, a semicarbazone or a hydrazone. Its ketonic nature is, however, established by reducing it to $\beta\beta\delta\delta$ *tetramethylpentan-γ-ol*, b. p. 165—166°, m. p. 50°, the *phenylurethane* of which has m. p. 118—119°, whilst the *formate* has b. p. 185°. In a similar manner, pentamethylacetone can be converted into $\beta\beta\delta\delta$ *tetra methylhexan-γ-one*, $CMe_3 \cdot CO \cdot CMe_2Et$, b. p. 172—174°, by the successive action of sodamide and ethyl bromide or iodide in benzene solution. Like its lower homologue, this substance forms neither oxime, semicarbazone or hydrazone. Reduction converts it into $\beta\beta\delta\delta$-*tetramethylhexan-γ ol*, $CMe_3 \cdot CH(OH) \cdot CMe_2Et$, b. p. 187—188°, the *phenylurethane* of which forms slender needles, m. p. 94—95°.

The ethylation of pinacoline can be effected in a precisely similar manner. The successive action of sodamide and ethyl bromide or iodide on an ethereal solution of pinacoline leads to the isolation of $\beta\beta$-*dimethylhexan-γ-one*, $CMe_3 \cdot CO \cdot CH_2 \cdot CH_2Me$, b. p. 146—148°, D_4^{25} 0·81055, n_α^{25} 1·40740, n_D^{25} 1·40952, n_β^{27} 1·41465, n_γ^{10} 1·41888, and $\beta\beta$-*dimethyl-δ-ethylhexan-γ-one*, $CMe_3 \cdot CO \cdot CHEt_2$, b. p. 171—176°, D_4^{25} 0·82521, n_α^{25} 1·42007, n_D^{25} 1·42227, n_β^{10} 1·42738, n_γ^{27} 1·43173. The former yields an *oxime*, needles, m. p. 76—77°, and on reduction gives $\beta\beta$-*dimethylhexan-γ-ol*, b. p. 155—157° (*phenylurethane*, m. p. 70—71°). The latter does not combine with hydroxylamine or with semicarbazide, but, when reduced with sodium and absolute alcohol, forms

$\beta\beta$ *dimethyl-δ-ethylhexan-γ-ol.* b. p. 187°, the *phenylurethane* of which crystallises with $\frac{1}{2}H_2O$ and has m. p. 107°. In benzene, or better in toluene solution, complete ethylation of pinacoline can be effected, whereby *$\beta\beta$-dimethyl-$\delta\delta$-diethylhexan-γ-one*, b. p. 214—216°, is produced. It does not yield an oxime or a semicarbazone. Reduction converts it into *$\beta\beta$-dimethyl-$\delta\delta$-diethylhexan-γ-ol*, $CMe_3 \cdot CH(OH) \cdot CEt_3$, b. p. 226—228°, the *phenylurethane* of which has m. p. 110°.

$\beta\beta\delta$-Trimethylhexan-γ-one, $CMe_3 \cdot CO \cdot CHMeEt$, b. p. 155—156°, is obtained mixed with unchanged starting material by the methylation of ethylpinacoline in ethereal solution. Since a separation of the two could not be effected by distillation, the product was treated with an alcoholic solution of hydroxylamine hydrochloride with which only the latter reacted to form an oxime. The mother liquors, separated as completely as possible from the crystalline oxime, were acted on by phenylcarbimide, whereby the dissolved oxime was converted into carbanilidoxime, which remained on distilling the mixture under diminished pressure. The distillate was treated with water to decompose the excess of phenylcarbimide, and the ketone extracted with ether and distilled. When reduced, it is converted into *$\beta\beta\delta$ trimethylhexan-γ-ol*, $CMe_3 \cdot CH(OH) \cdot CHMeEt$, b. p. 169°, the *phenylurethane* of which has m. p. 78°.

$\beta\beta\epsilon$-Trimethylhexan-γ-one, $CMe_3 \cdot CO \cdot CH_2 \cdot CHMe_2$ (compare Nef, A., 1902, i. 6), is obtained in the usual manner as a liquid, b. p. 157·5—158 5°. Its oxime has m. p. 77—78°, whereas Nef gives 66—70°.

Although the action of allyl iodide on the sodium derivative of acetophenone yields only complex resinous products, allylpinacolines can be readily obtained by the successive action of sodamide and allyl iodide on an ethereal solution of pinacoline. In this manner, *allylpinacoline*, $CMe_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH:CH_2$, b. p. 61—64°/14 mm., and *diallylpinacoline*, $CMe_3 \cdot CO \cdot CH(CH_2 \cdot CH:CH_2)_2$, b. p. 83—86°/14 mm., are readily prepared.

δ-Benzyl-$\beta\beta$-dimethyl-δ-ethylhexane-γ-one, $CMe_3 \cdot CO \cdot CEt_2 \cdot CH_2Ph$, is obtained by the action of benzyl chloride on a boiling solution of the sodium derivative of diethylpinacoline in toluene. It has b. p. 152—154°/15 mm., and does not yield an oxime or a semicarbazone.

In the cases of pinacoline and of acetophenone, a tertiary carbon atom is attached to the carbonyl group. The authors have therefore extended their investigations to such ketones in which this is not the case, and find that alkylation can be similarly effected, substitution occurring at either of the secondary carbon atoms attached to the keto-group (compare Haller, A., 1905, i, 214; Haller and Bauer, A., 1912, i, 269).

An ethereal solution of diethyl ketone reacts vigorously with sodamide, and, after addition of methyl iodide, yields, on fractionation, *ethyl isopropyl ketone*, $COEt \cdot CHMe_2$, b. p. 115—119°, di-*isopropyl* ketone, $CO(CHMe_2)_2$, b. p. 123—124·5° (*semicarbazone*, m. p. 143—144°), and a *fraction*, b. p. 148—152°/18 mm., which is probably *$\delta\zeta$-dimethyl-$\gamma\eta$-diethyl-$\Delta^{\gamma\zeta}$-nonadien-ϵ-one*,

$$CEt_2 : CMe \cdot CO \cdot CMe : CEt_2.$$

$\beta\delta\delta$-Trimethylhexan-γ-one, b. p. 158—161°, is prepared by the

ethylation of di-*iso*propyl ketone in ethereal solution. It does not yield an oxime or a semicarbazone. On reduction it gives $\beta\delta\delta$ *trimethylhexan-γ-ol*, $CMe_2 \cdot CH(OH) \cdot CMe_2Et$, b. p. 170—171°, the *phenylurethane* of which has m. p. 64°. γγεε-*Tetramethylheptan-δ-one*,

$$CMe_2Et \cdot CO \cdot CMe_2Et,$$

prepared by the ethylation of *iso*propyl *tert.*-amyl ketone in benzene solution, has b. p. 196—198°, and does not give an oxime or a semicarbazone. Sodium and absolute alcohol convert it into γγεε-*tetramethylheptan-δ-ol*, b. p. 210—212° (*phenylurethane*, m. p. 62—63°).

By repeated methylation of *iso*valerone in benzene solution and subsequent fractional distillation, the following products have been obtained : (i) $\beta\gamma\epsilon\zeta$-*tetramethylheptan-δ-one*,

$$CHMe_2 \cdot CHMe \cdot CO \cdot CHMe \cdot CHMe_2,$$

b. p. 76—78°/13 mm., which, when energetically treated, appears to yield small quantities of the corresponding *oxime*; (ii) $\beta\gamma\gamma\epsilon\zeta$-*pentamethylheptan-δ-one*, $CHMe_2 \cdot CHMe \cdot CO \cdot CMe_2 \cdot CHMe_2$, b. p. 88—89°/13 mm., which does not yield an oxime when heated with Crismer's reagent in alcoholic solution. $\beta\gamma\gamma\epsilon\epsilon\zeta$-*Hexamethylheptan-δ-one*,

$$CHMe_2 \cdot CMe_2 \cdot CO \cdot CMe_2 \cdot CHMe_2,$$
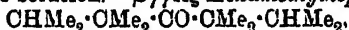
b. p. 107—109°/14 mm., is prepared by the methylation of trimethyl-*iso*valerone in toluene solution. When reduced with sodium and alcohol, it yields a small quantity of a *substance* which behaves like an unsaturated hydrocarbon, and $\beta\gamma\gamma\epsilon\epsilon\zeta$-*hexamethylheptan-δ-ol*,

$$CHMe_2 \cdot CMe_2 \cdot CH(OH) \cdot CMe_2 \cdot CHMe_2,$$

b. p. 115—117°/13 mm. (*phenylurethane*, m. p. 91—92°).

H. W.

Optically Active Complex Glucinum Sugar Compounds. BENNO BLEYER and L. PACZUSKI (*Zeitsch. physikal. Chem.*, 1913, **84**, 1—14).—The authors have determined the influence of an alkaline solution of glucinum hydroxide on the rotatory power of mannitol. It is shown that when an alkaline solution of glucinum hydroxide is added to a solution of inactive mannitol, the solution becomes markedly lævorotatory. The influence of the alkaline glucinum solution is shown to depend on the presence of GlO_2'' ions in the solution, that is, it is due to sodium glucinate. The presence of glucinum hydroxide as a colloid could not produce so large a change in the rotation. A method is worked out, depending on the change of rotation, for determining the relative strength of the acid in amphoteric metal hydroxides. On adding solutions of sodium glucinate to mannitol, a condition is reached at which a constant rotation is reached ; further additions cannot change this in either sense. This condition is reached when the concentration 13·84 grams mannitol, 72 grams sodium hydroxide, and 56·64 grams of glucinum sulphate per litre of solution is reached. A complex compound is formed by the action of sodium glucinate on mannitol, which is not hydrolysed at the concentrations examined, $(1/640—10/640)n$. This compound is similar to the complex glucinum hydroxydicarboxylic acid of Rosenheim and Itzig (A., 1899, i, 739).

J. F. S.

Unfermentable Residue in Hydrolytic Products of Starch.
ARTHUR P. BRYANT and C. S. MINER (*Eighth Intern. Cong. App. Chem.*, 1912, 13, 57—61).—Results are recorded which tend to show that some of the hydrolytic products of starch, such as "grape-sugar" and "liquid glucose," contain *iso*maltose.   W. H. G.

Presence of Maltose in Acid Hydrolysed Starch Products.
GEORGE DEFREN (*Eighth Intern. Cong. App. Chem.*, 1912, 13, 111—112). —It has been found possible to isolate maltose from a crude glucose obtained by the hydrolysis of starch with acids. The dextrose present in the crude product was removed by fermentation, making use of *Saccharomyces apiculatus*, and the dextrin separated from the maltose subsequently by fractional precipitation with alcohol.   W. H. G.

Hydrolysis of Starch by Acids with Some Additional Results. on the Speed of Hydrolysis. GEORGE DEFREN (*Eighth Intern. Cong. App. Chem.*, 1912, 13, 113—123).—An investigation on the hydrolysis of starch by acids. The relative speeds of hydrolysis using hydrochloric, sulphuric, oxalic, sulphurous and acetic acids are given, likewise results which show the effect of the concentration of the acid and the temperature on the rate of hydrolysis. The increase in the rate of hydrolysis with rise of temperature above 100° is very great, indicating that the starch molecule becomes very "labile" at these temperatures.   W. H. G.

Osmotic Pressure of Colloids. V. Colloid Chemistry of the Dextrins. WILHELM BILTZ (and WILHELM TRUTHE) (*Zeitsch. physikal. Chem.*, 1913, 83, 683—707. Compare A., 1910, ii, 22, 673 ; 1911, ii, 702 ; this vol., i, 593).—The molecular weight of a number of dextrins is determined by extrapolation to concentration zero from the calculated molecular weights obtained from the measurement of the osmotic pressure of dilute solutions. It is shown that even in dilute solutions the dextrins associate very markedly. The following values are found for the molecular weights: amylodextrin (*a*) 22200, amylodextrin (*b*) 20500, achroodextrin 10200. diastase dextrin (from grain) 11700, diastase dextrin (from beer) 8200, erythrodextrin 6800, erythrodextrin IIa 3000, acid dextrin 4000, achroodextrin I 1800, achroodextrin II 1200, dextrin β 950, sucrose 340, commercial dextrin (2 specimens) 5000, 6000, specially purified commercial dextrin 2800 and 2700. dextrin purified by dialysis 6200. The gold numbers of the various dextrins are determined, and it is shown that a relationship exists between the molecular weight and the gold number ; generally a small gold number accompanies a large molecular weight. The authors have shown that in many cases the dextrins possess more than one gold number, and that there is an oscillating protecting action of the colloid between given concentrations. The viscosity of the dextrins in dilute solutions, that is, up to 5%, is determined, and it is shown that a parallelism exists between the viscosity and the molecular weight. It is also shown that the higher the molecular weight, the more the dextrins are adsorbed by ferric hydroxide gels.   J. F. S.

Hydrolysis and Acetolysis of Cellulose. HERMANN OST (*Annalen*, 1913, **398**, 313—343. Compare this vol., i, 446).—The composition of the hydrocelluloses obtained as the initial product of the hydrolysis of cellulose by dilute mineral acids has long been a matter of dispute. The author finds that cellulose can be dried completely, without discoloration, by heating slowly to 100° and finally at 120—125°; the same is true of hydrocelluloses, some specimens of which, however, become discoloured at 125—150°. Since the ultimate analysis of completely dried cellulose and hydrocelluloses fails to disclose any differences in the percentages of carbon and of hydrogen, the author abandons his previous views that hydrocelluloses are hydrated celluloses, and inclines to Stern's opinion (T., 1904, **85**, 336) that there is no difference in the composition of celluloses and hydrocelluloses. The molecular magnitude of the latter is the smaller, as is indicated, not only by the smaller viscosity of their solutions, but also by their greater reducing action on copper salts, hydroxyl or aldehydo-groups being produced during the hydrolysis of the cellulose.

The acetolysis of cellulose is described in detail, the conditions under which cellobiose octa-acetate or dextrose a-penta-acetate (Ost, *loc. cit.*) are produced being definitely determined. The uncrystallisable syrup obtained in the acetolysis of cellulose resembles that obtained in the acetolysis of dextrose in acetic acid content, in rotatory power, and in yielding crystallised dextrose a-penta-acetate by further acetylation. Both syrups consist essentially of dextrose acetates mixed with acetates of *iso*maltose and dextrins and of other foreign substances.

The total yield of dextrose and cellobiose acetates obtained by the acetolysis of cellulose is 90% of that theoretically possible. Acetolysis, therefore, furnishes another proof that the cellulose molecule is composed only of dextrose residues.   C. S.

Absorption Spectra of the Copper Derivatives of Primary Aliphatic Nitroamines. ANTOINE P. N. FRANCHIMONT and HILMAR J. BACKER (*Rec. trav. chim.*, 1913, **32**, 158—163. Compare T., 1912, **101**, 2256).—The authors have examined the absorption spectra of aqueous solutions of the copper salts of methylnitroamine, ethylnitroamine, ethylnitrosohydroxylamine, of copper nitrate and ammoniacal copper nitrate at equivalent concentrations. The copper salts of the nitroamines are much more strongly absorbent than a solution of copper nitrate with the same copper content, whilst the light which is not absorbed is less violet than in the case of the copper salt of ethylnitrosohydroxylamine. The spectra of the copper salts of methyl- and ethyl-nitroamines are practically identical, and do not show an absorption band.

The electrical conductivity of solutions of the copper salts of nitroamines is noticeably less than that of their sodium salts or of ordinary copper salts. The copper salt of ethylnitrosohydroxylamine conducts still more feebly.

Solutions of the copper salts of nitroamines give the ordinary reactions for copper, whilst that of ethylnitrosohydroxylamine, although yielding precipitates with sodium hydroxide and with

hydrogen sulphide, gives only a brown coloration with potassium ferrocyanide.

The authors are led to the conclusion that the copper derivative of ethylnitrosohydroxylamine is probably a complex internal salt, but in view of the differences existing between this substance and the copper salts of the nitroamines, hesitate to assign a similar structure to the latter substances, although their intense colour and feeble electrical conductivity point to a relationship between the metal and nitrogen.

H. W.

Oxalyl Derivatives of Amino-acids.   D. J. MEYERINGH (*Rec. trav. chim.*, 1913, **32**, 140—157).—The author has prepared a series of oxalyl derivatives of amino-acids which contain the residues of two different amino-acids, by the action of ethyl chloroglyoxylate on the hydrochloride of the ester of an amino-acid, followed by treatment of the product so obtained with the potassium salt of a second amino-acid.

Ethyl chloroglyoxylate is best obtained by heating a mixture of equimolecular quantities of ethyl oxalate and phosphorus pentachloride until evolution of ethyl chloride ceases. It has b. p. 135°.

Methyl oxamidodiacetate, $C_2O_2(NH·CH_2·CO_2Me)_2$, has m. p. 158·5°, instead of 139—140° recorded by Kerp and Unger (A., 1897, i, 269).

Oxamidoacetic acid, $NH_2·CO·CO·NH·CH_2·CO_2H$, is obtained from oxamethane and potassium aminoacetate according to the method of Kerp and Unger (*loc. cit.*). The corresponding *methyl* ester, m. p. 157°, is obtained by treatment of the *silver* salt with an excess of methyl iodide and is converted by ammonia into the *amide*, needles, m. p. 251—252° (decomp.).

Ethyl ethoxalylaminoacetate, $CO_2Et·CO·NH·CH_2·CO_2Et$, b. p. 188°/18 mm., m. p. 16°, is prepared in 84% yield by heating an equimolecular mixture of ethoxalyl chloride and ethyl aminoacetate hydrochloride in dry benzene until evolution of hydrogen chloride ceases. It is converted by ammonia into the corresponding di-amide.

Methyl ethoxalyl-a-aminopropionate, $CO_2Et·CO·NH·CHMe·CO_2Me$, b. p. 173·5°/19 mm., is similarly prepared from ethyl chloroglyoxylate and methyl a-aminopropionate hydrochloride. The *diamide*, prepared by means of liquid ammonia, forms slender needles, m. p. 216·5°. No evidence of the formation of an isomeric diamide could be obtained.

Methyl glycineoxalyl-a-aminopropionate,

$$CO_2H·CH_2·NH·CO·CO·NH·CHMe·CO_2Me,$$

m. p. 136—137°, is prepared by the addition of methyl ethoxalyl-a-aminopropionate to a solution of potassium aminoacetate, care being taken that the temperature does not exceed 5°. At higher temperatures, and in the presence of excess of alkali, the ester is readily saponified, the corresponding *acid* decomposing at 210° when rapidly heated.

When a solution of a-alanine in potassium hydroxide is added to ethyl ethoxalylglycine, *ethyl a-alanineoxalylglycine*,

$$CO_2H·CHMe·NH·CO·CO·NH·CH_2·CO_2Et,$$

m. p. 142·5°, is obtained if the temperature does not rise above 5°. At higher temperatures, and in the presence of more concentrated potassium hydroxide, alanine separates and the potassium salt of ethyl

oxalylaminoacetate is produced. In alcoholic solution, alanine always separates to some extent, and the *potassium* salt of *ethyl a alanineoxalylglycine* is obtained.

Dimethyl a-alanineoxalylglycine,
$$CO_2Me \cdot CHMe \cdot NH \cdot CO \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Me,$$
m. p. 98·5°, is prepared by saturating a methyl alcoholic solution of methyl glycine oxalyl-a-aminopropionate with hydrogen chloride. *Methyl ethyl a-alanineoxalylglycine,*
$$CO_2Me \cdot CHMe \cdot NH \cdot CO \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et,$$
m. p. 106°, is formed by similar treatment of a methyl alcoholic solution of ethyl a-alanineoxalylglycine or of an ethyl alcoholic solution of methyl glycineoxalyl-a-aminopropionate, whilst *diethyl a-alanineoxalylglycine,* $CO_2Et \cdot CHMe \cdot NH \cdot CO \cdot CO \cdot NH \cdot CH_2 \cdot CO_2Et$, m. p. 120°, is similarly produced from ethyl a-alanineoxalylglycine or from the corresponding free acid.

a-Alanineoxalylglycinediamide,
$$NH_2 \cdot CO \cdot CHMe \cdot NH \cdot CO \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot NH_2,$$
m. p. 272—274° (decomp.), is obtained by the action of liquid ammonia on dimethyl a-alanineoxalylglycine.

a-Aminoisobutyric acid does not react with ethyl ethoxalylglycine in the presence of the calculated quantity of potassium hydroxide at 0°.

Methyl ethoxalyl-a-phenylaminoacetate, $CO_2Et \cdot CO \cdot NH \cdot CHPh \cdot CO_2Me,$ m. p. 56°, is prepared by heating ethyl chloroglyoxylate and methyl a-phenylaminoacetate hydrochloride in benzene solution. The corresponding *diamide* has m. p. 229°. By the action of oxalyl chloride (1 mol.) on methyl a-phenylaminoacetate hydrochloride in dry benzene, two isomeric *forms* of dimethyl oxalyldi (a-phenylaminoacetate), $C_2O_2(NH \cdot CHPh \cdot CO_2Me)_2,$ are obtained which may be separated by taking advantage of their different solubilities in benzene. They have m. p. 169—170° and 195° respectively.

Unsuccessful attempts have been made to prepare acetyl and nitro-derivatives of several of the above substances.

The presence of the oxalyl group has been actually ascertained in each of the above derivatives. They have further been examined with regard to their ability to give the biuret reaction. It appears that only those substances show this reaction in which at least one of the amino-groups is intact. H. W.

Nitriles of Diaminodimethyl- and Diaminomethylethyl-succinic Acids and their Behaviour on Hydrolysis. OTTO DIELS and HAJIME OTSUKI (*Ber.,* 1913. **46,** 1877—1983).—The cyanohydrins of dimethyl diketone and methyl ethyl diketone react with ammonia, yielding the nitriles of diaminodimethyl- and diaminomethylethyl-succinic acids which, on hydrolysis with hydrochloric acid, are converted into compounds $C_6H_8N_2Cl$ and $C_7H_{10}N_2Cl$ respectively. The constitution of the latter compounds has not been definitely established, but from their pronounced basic properties and their behaviour toward nitrous acid, the conclusion is drawn that they contain only one amino-group. The halogen atom is very firmly attached, and cannot be removed by any of the usual reagents.

When treated with nitric acid, the compounds are completely decomposed, yielding a chloro-nitromethane. The formation of the latter compound indicates that the halogen is attached to one of the carbon atoms.

Methyl ethyl diketone cyanohydrin, OH·CMe(CN)·CEt(CN)·OH, is prepared by the action of hydrogen cyanide in ethereal solution on methyl ethyl diketone in the presence of potassium carbonate. It forms small, hygroscopic, crystalline plates, m. p. 76°, and when heated for five minutes with strong nitric acid is transformed into an *isomeride*, which sinters at 100°, m. p 103°.

Diaminomethylethylsuccinonitrile, NH₂·CMe(CN)·CEt(CN)·NH₂, prepared by the action of concentrated aqueous ammonia on the preceding cyanohydrin at 0°, crystallises in hexagonal platelets or needles, m. p. 68°, and when maintained at 37° for two days with concentrated hydrochloric acid yields the *compound*, $C_7H_{10}N_3Cl$, which crystallises in lustrous, slender needles, m. p. 77·5°, forms a crystalline *hydrochloride* and *sulphate*, and on treatment with nitrous acid is converted into a *hydroxy*-compound, $C_7H_9ON_2Cl$, m. p. 147°.

s-*Diaminodimethylsuccinonitrile*, NH₂·CMe(CN)·CMe(CN)·NH₂, prepared from diacetylcyanohydrin (A., 1912, i, 942) and strong aqueous ammonia at 0°, crystallises in plates or leaflets, m. p. 166·5°. It is accompanied by a *substance*, $C_{12}H_{20}O_3N_6$, which forms small, tabular crystals, m. p. 234° (decomp.). On hydrolysis with concentrated hydrochloric acid at 37°, it yields the *compound*, $C_6H_8N_3Cl$. This forms long, lustrous needles, m. p. 140·5°, and is converted by the action of nitrous acid into a *hydroxy*-compound, $C_6H_7ON_2Cl$, which crystallises in lustrous needles, m. p. 227°, and when methylated by means of aqueous potassium hydroxide and methyl sulphate yields a *methyl ether*, $C_7H_9ON_2Cl$, crystallising in needles, m. p. 96°; if the methylation is carried out with diazomethane, an isomeric *methyl ether* of m. p. 54—55° is obtained.   F. B.

The Origin of Optically Active Compounds in the Living Cell; the Artificial Preparation of Optically Active Compounds Without the Intervention of Asymmetrical Molecules or Asymmetrical Forces. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1913, **52**, 439—470).—In compounds of the type $C(R_1R_2R_3)$—$C(R_4R_5R_6)$ there are, according to van't Hoff, twelve isomerides possible, of which eight can be derived from the four others, simply by rotation about the C—C axis. Isomerides which can be derived from one another simply by a rotation of this description are designated by the author as "relative isomerides" in contradistinction to the isomerides ("bond-isomerides") which can only be derived from one another by changes in the bonds uniting the R groups. If the assumption is made that mirror images have the same solubilities as one another, they are not separable from one another by fractional crystallisation. If, however, a racemic mixture containing the two mirror images can be subjected to such treatment that the antipodes can be converted into their "relative isomerides," then it is possible that the two constituents can change at different rates, or that the rotation about the C—C axis can take place in opposite directions. If, therefore, it is possible, by any

method, to produce "relative isomerides" in a racemic mixture, then it is also conceivable that a mixture can be produced which contains isomerides which are no longer mirror images of one another, and which are postulated to be separable from one another by a process of fractional crystallisation. The author in conjunction with G. Hilgendorff has applied the above conceptions to the investigation of the asparagines. He confirms the observations of Piutti, that a mixture of the *d*- and *l*-substances can be separated by crystallisation from hot water. He shows, furthermore, that a mixture, in equimolar proportions, of these two isomerides has double the solubility of either constituent separately, and that by recrystallisation at 20° the two constituents are not separable from one another. If, however, the mixture is first heated with water for some hours, subsequent fractional crystallisation can yield crops of crystals, which rotate light in the opposite direction. It is assumed here that, in accordance with the theory given above, the isomerides which form mirror images are converted into "relative isomerides" by the action of heat which are no longer mirror images. Copper salts were also obtained by fractional crystallisation from the mixture of the heated acids, of which the various fractions differed markedly from one another both in colour and solubilities. An attempt to obtain optically active isomerides in a similar way from racemic acid failed. It is pointed out, however, that when the *d*- and *l*-tartaric acids are combined there is development of heat, and a product of higher melting point, and less soluble in water than either the *d*- or *l*-acids, is obtained ; in the case of combination of the *d*- and *l*-asparagines no heat is developed, and the product is more soluble than the antipodes and has a lower m. p. Apparently a true racemic combination is not produced in this case. The action of heat on the sodium–ammonium salt of racemic acid led, however, to a very partial separation into optically active isomerides. It is claimed that the experiments described above afford the first examples of the production of optically active substances without intervention of asymmetrical substances and forces, and the biological significance of the results is discussed in some detail.

S. B. S.

Preparation of Carbonyl Cyanide. DANIEL BERTHELOT and HENRY GAUDÉCHON (*Compt. rend.*, 1913, 156, 1990—1992. Compare this vol., i, 715).—It has already been shown that, in a manner analogous to the combination with chlorine, hydrogen and ammonia producing carbonyl chloride, formaldehyde and formamide respectively, carbon monoxide undergoes combination with cyanogen if a mixture is exposed to ultra-violet light, yielding carbonyl cyanide, CN·CO·CN.

Endeavours to prepare this substance by other methods reveal the fact that the silent electric discharge, which, although it frequently causes similar effects to ultra-violet light, exerts a quite distinct effect in other cases, also gives rise to a combination of the two gases. The mixture may contain varying proportions of the gases as long as neither becomes exhausted, but the action is most rapid when equal volumes are applied. With a tension of 6000 volts combination occurs much more rapidly than in ultra-violet light, and in one experiment

a mixture of 5 c.c. of carbon monoxide with an approximately equal volume of cyanogen gave a contraction of 3 c.c. in ten minutes. The yellow solid product is partly soluble in water and wholly soluble in alkalis. From the slow rate of its hydrolysis by dilute sulphuric acid, the substance evidently represents an even higher stage in the polymerisation of the simple molecule $CN \cdot CO \cdot CN$ than the product of ultra-violet illumination.

Attempts were made to prepare the unpolymerised substance by chemical processes, such as the action of carbonyl chloride on cyanide of silver or mercury, or from carbon monoxide and cyanogen by mere heating, but the results were consistently negative.

<div align="right">D. F. T.</div>

Some Complex Copper Alkali Ferrocyanides. KSHITIBHUSAN BHADURI and SARASHILAL SARKAR (*Zeitsch. anorg. Chem.*, 1913, **82**, 164—172).—Dextrose is added to a solution of potassium ferro-cyanide, which is then mixed with Fehling's solution. A cream-coloured precipitate is obtained, which is crystalline if the solutions are dilute. It is washed with boiling water and dried in a vacuum over sulphuric acid. It becomes violet and blue with sulphuric acid, and yields a nitroprusside with nitric acid. The crystalline characters are described. The formula of the original salt is
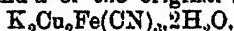
$$K_2Cu_2Fe(CN)_9, 2H_2O,$$

the blue salt being $K_3Cu_3Fe(CN)_9, K_2Cu[Fe(CN)_6]_2$, and the nitro-prusside, $K_2Fe(CN)_5 \cdot NO, 2Cu_2Fe(CN)_5 \cdot NO, 13H_2O$. Alkali yields a compound $K_2CuFe(CN)_6, CuO, 3\frac{1}{2}H_2O$. *Lithium copper ferrocyanide*, $Li_2Cu_2Fe(CN)_8, 4H_2O$, is lemon-yellow, and the sodium compound has also been obtained. The *ammonium* salt is obtained by dissolving cupric oxide in ammonia, and adding dextrose and ammonium ferro-cyanide, giving a red precipitate, $(NH_4)_2Cu_2Fe(CN)_6, 3NH_3$, and, from the filtrate, pale blue crystals of $(NH_4)_8Cu_5[Fe(CN)_6]_3, 8NH_3$. The compounds $2CuK_2Fe(CN)_6, 8CuO, 16H_2O$ and

$$(NH_4)_8Cu_4KFe_2(CN)_{12}, 5NH_3$$
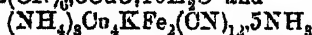
have also been obtained. When copper sulphate is added to potassium ferricyanide and the precipitate is dissolved in ammonia, brown crystals of ammoniacal cupric ferrocyanide are obtained,

$$Cu_3Fe(CN)_6, 3NH_3.$$
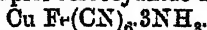
The nature of the reduction process is unknown.

<div align="right">C. H. D.</div>

The Action of Different Metals on Potassium Ferricyanide Solutions. GEORGE McPHAIL SMITH [and RALPH ATKINSON LYNCH] (*Zeitsch. anorg. Chem.*, 1913, **82**, 63—70. Compare Beutel, A., 1912, i, 543).—Powdered iron prepared by reduction reduces potassium ferricyanide in an atmosphere of hydrogen:

$$4K_3Fe(CN)_6 + 2Fe = Fe_2Fe(CN)_6 + 3K_4Fe(CN)_6.$$
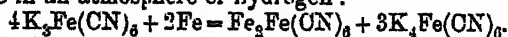
Nickel and zinc also reduce to ferrocyanide without passing into solution, and form precipitates. Silver reacts in the cold:

$$4K_3Fe(CN)_6 + 4Ag = Ag_4Fe(CN)_6 + 3K_4Fe(CN)_6,$$
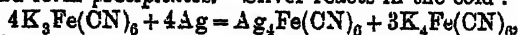
but at $100°$ silver goes into solution as a complex salt. With mercury, metallic iron is first formed: $2K_3Fe(CN)_6 + 3Hg = 3K_2Hg(CN)_4 + 2Fe.$ This iron then reacts as above, and, in presence of alkali hydroxide,

ferric hydroxide is ultimately formed. Gold dissolves slowly in ferricyanide solutions.

[With MICHELE CROCE.]—Silver ferrocyanide dissolves in potassium ferrocyanide solution, forming potassium silver cyanide, $KAg(CN)_2$.

C. H. D.

Univalent Nickel Compounds. II. ITALO BELLUCCI and R. CORELLI (*Atti R. Accad. Lincei*, 1913, [v]. 22, i, 703—708. Compare this vol., ii, 604).—Continuing their work on the nature of the compound contained in the red liquid obtained by the reduction of potassium nickelocyanide, the authors criticise adversely the second also of the analytical methods employed by Moore (*loc cit.*), so that they reject the formula Ni_3X_2 proposed by that author. By three analytical methods they obtain concordant results indicating that the red solution contains a cyano-salt in which nickel is univalent. The analytical methods employed were : (1) the measurement of the amount of hydrogen evolved by the solution in the warm ; (2) titration with $N/10$-iodine solution ; (3) titration with a standard hydrogen peroxide solution.

R. V. S.

New Compounds and Scissions of Azodicarboxylic Acid. OTTO DIELS and MAX PAQUIN (*Ber.*, 1913, 46, 2000—2013).—The decomposition of derivatives of azodicarboxylic acid on dehydration, hydrolysis or heating is described. When azodicarboxylamide is heated with phosphoric oxide, nitrogen, water, cyanic acid and hydrogen cyanide are formed, according to the equation :

$$N_2(CONH_2)_2 = H_2O + N_2 + HCNO + HCN.$$
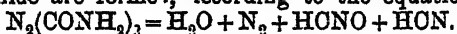
Substituted azoamides, such as azodicarboxyldiethylamide, yield *iso*-cyanates and *iso*nitriles : $N_2(CO\cdot NHEt)_2 = H_2O + N_2 + C_2H_5NCO + C_2H_5NC$. The same compound also readily forms a brick-red *silver* salt which decomposes at 141°, or when treated with iodine, into ethylcarbimide : $N_2(CO\cdot NAgEt)_2 = 2Ag + N_2 + 2CO\colon NEt$;

$$N_2(CO\cdot NAgEt)_2 + I_2 = 2AgI + N_2 + 2CO\colon NEt.$$
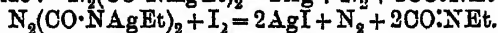
When azodicarboxylamide is heated with concentrated sulphuric acid, it decomposes into carbon dioxide, carbon monoxide, sulphur dioxide and nitrogen, but, in the cold, hydrazine sulphate and hydrazoic acid are formed. When boiled with dilute sulphuric acid, the compound gives a larger yield of hydrazoic acid, the other products including carbon monoxide, carbon dioxide, nitrogen and hydrazine and ammonium sulphates. Angeli (A., 1910, ii, 844) observed the production of hydrazoic acid under these conditions from azodicarboxylic acid itself, and explained it by assuming that di-imine, $NH\colon NH$, is first formed, and that it polymerises to the hypothetical tetrazen, which may decompose in two ways :

$$2NH\colon NH \longrightarrow NH_2\cdot N\colon N\cdot NH_2 \longrightarrow NH_3 + N_3H \text{ or } N_2 + N_2H_4.$$
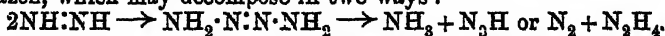
The primary decomposition of azodicarboxylamide might also follow two courses :

$$N_2(CO\cdot NH_2)_2 + 2H_2O = 2CO_2 + 2NH_3 + NH\colon NH \text{ or}$$
$$N_2(CO\cdot NH_2)_2 = 2CO + NH_2\cdot N\colon N\cdot NH_2.$$
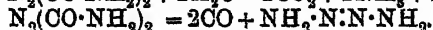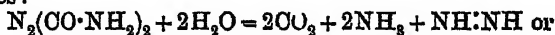
Methyl hydrazodicarboxylate, $N_2H_2(CO_2Me)_2$, was obtained in radiating bundles of broad needles by the action of methyl chloroformate on

hydrazine hydrate, and oxidised by concentrated nitric acid to *methyl azodicarboxylate*. The latter has b. p. 85°/7 mm., is hydrolysed by water to the hydrazo-ester, carbon dioxide and hydrazoic acid, and is oxidised by fuming nitric acid to oxalic acid.

Whereas primary amines convert the esters of azodicarboxylic acid into amides, secondary and tertiary amines usually form additive compounds which, on hydrolysis with dilute acids, yield the corresponding hydrazo-esters together with aldehydes and amines which contain one radicle less attached to the nitrogen atom than the original amine does. Thus the *compound* of ethyl azodicarboxylate with dimethylamine yields ethyl hydrazodicarboxylate, formaldehyde and methylamine, its constitution being therefore represented by the formula $CO_2Et\cdot N(CH_2\cdot NHMe)\cdot NH\cdot CO_2Et$. The compound forms well-defined prisms or rhombic plates, m. p. 95°, decomposes, when the aqueous solution is boiled, into ethyl hydrazodicarboxylate, dimethylamine, nitrogen and carbon dioxide, and is oxidised by nitric acid to ethyl azodicarboxylate. When submitted to dry distillation, it decomposes vigorously, giving a good yield of hydrazomethane, together with ethyl hydrazodicarboxylate, ethylcarbimide and formaldehyde :

$$2CO_2Et\cdot N(CH_2\cdot NHMe)\cdot NH\cdot CO_2Et =$$
$$2CH_2O + 2CO:NEt + N_2H_2(CO_2Et)_2 + N_2H_2Me_2.$$
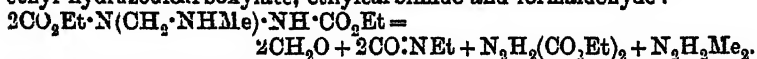
When the decomposition and distillation are carried out under reduced pressure, however, the chief product is ethyl dimethylcarbamate :

$$2CO_2Et\cdot N(CH_2\cdot NHMe)\cdot NH\cdot CO_2Et = N_2 + EtOH + CO + NMe\cdot CO_2Et.$$

The latter was characterised by conversion into methylnitroamine (Franchimont and Klobbie, A., 1889, 492).
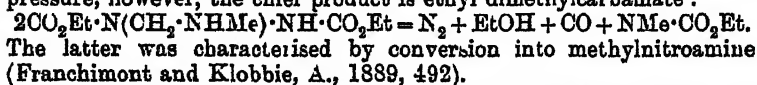
The *compound*, $CO_2Et\cdot N(CHMe\cdot NHEt)\cdot NH\cdot CO_2Et$, prepared by mixing ethyl azodicarboxylate with diethylamine, forms clusters of needles, m. p. 68°, is sparingly soluble in cold water or water at 80—90°, but is readily soluble at 50°, and yields acetaldehyde on hydrolysis. The *compound*, $CO_2Me\cdot N(CH_2\cdot NMePh)\cdot NH\cdot CO_2Me$, obtained from methyl azodicarboxylate and dimethylaniline, crystallises from ether in prismatic columns and rhombic plates, m. p. 95—96°, and yields formaldehyde, methylaniline, and methyl hydrazodicarboxylate on hydrolysis. The *compound*,

$$NHEt\cdot CO\cdot N(CH_2\cdot NHMe)\cdot NH\cdot CO\cdot NHEt,$$

prepared by mixing azodicarboxylethylamide with ether and dimethylamine in the cold in a sealed tube, forms rhombic plates, m. p. 109—111° (decomp.), and yields formaldehyde on hydrolysis.

J. C. W.

1 : 1-Dimethyl*cyclo*hexane. NICOLAI D. ZELINSKI and NICOLAI N. LEPESCHKIN (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 613—616).— β-Methyl-Δ²-hepten-ζ-one was converted into the η-acetyl derivative, the latter transformed by the action of sulphuric acid into 6-acetyl-1 : 1-dimethyl*cyclo*hexan-5-one, and this hydrolysed to 1 : 1-dimethyl-*cyclo*hexan-5-one, which, on reduction in ethereal solution by means of sodium and water, gave 1 : 1-*dimethylcyclohexan-5-ol*,

$$CH_2\begin{array}{c}CH(OH)\cdot CH_2\\CH_2 ----- CH_2\end{array}CMe_2,$$
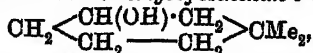
b. p. 185°/754 mm., D_4^{15} 0·9071, n_D^{15} 1·4558. Reduction of the

alcohol with hydriodic acid yields 1:1-dimethyl*cyclo*hexane, b. p. 119·2—119·7°, D_4^{16} 0·7843, D_1^{20} 0·7792, n_D^{16} 1·4320 (compare Crossley and Renouf, T., 1905, **87**, 1487). When treated with bromine in presence of aluminium bromide, this hydrocarbon is readily converted into tetrabromo-*p*-xylene, one of the methyl groups migrating to the para-position under the conditions of bromination (compare A., 1902, i, 143). T. H. P.

The Benzene Problem. KURT GEBHARD (*J. pr. Chem.*, 1913, ii], **88**, 94—96).—A reply to Liebig (this vol., i, 607). F. B.

A New Method for the Introduction of Iodine into Aromatic Substances. KARL ELBS and A. JAROSLAVZEV (*J. pr. Chem.*, 1913, [ii], **88**, 92—94).—Iodo-derivatives of aromatic hydrocarbons may be readily prepared by boiling the latter with iodine and sodium persulphate in glacial acetic acid solution. Thus benzene yields iodo- and *p*-di-iodobenzene, whilst toluene gives rise to *o*- and *p*-iodotoluenes.

The following iodo-compounds have also been prepared by this method : 4-iodo-*m*-xylene, 4-iodo-*o*-xylene, 2-iodo-*p*-xylene, and iodo-ψ-cumene.

s-*Di*-p-*iododiphenylethane*, prepared from dibenzyl, has m. p. 152° ; the position of the iodine atoms has been established by its oxidation to *p*-iodobenzoic acid by chromic acid in glacial acetic acid solution. F. B.

Some Aromatic Fluorine Compounds. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1913, 241—278).—The compounds described are mostly prepared by decomposing aromatic diazonium salts with hydrofluoric acid in vessels of silver or platinum. They were obtained for thermochemical investigations (compare A., 1907, ii, 9 ; 1908, ii, 354 ; 1909, ii, 297).

o-Fluoronitrobenzene could not be prepared : the para-isomeride forms colourless crystals, m. p. 27°, b. p. 205°/735 mm., and the *meta* derivative has m. p. 3·6°, b. p. 200°/756 mm., D_{17} 1·3272, n_D 1·5207.

1-Fluoro-2 : 4-dinitrobenzene forms large, colourless, hard crystals m. p. 25·8°, b. p. 178°/25 mm.

m-*Fluoroacetanilide* crystallises in large, colourless prisms, m. p. 84·5° ; the para-isomeride forms tiny needles, m. p. 152°. 4-*Fluoro*-3-*nitroacetanilide* separates in very pale yellow needles, m. p 138·5°.

p-*Fluorophenol*, prepared by heating fluorophenetole with aluminium chloride, has b. p. 185·5°. It forms transparent, tabular crystals, m. p. 26·5—27°, but this modification changes on keeping into a stable form, m. p. 45°, consisting of acicular crystals resembling phenol.

m-*Fluorophenol*, prepared by decomposing *m*-fluorobenzenediazonium sulphate, forms large, prismatic crystals, m. p. 13·7°. o-*Fluorophenol*, b. p. 151—152°, m. p. 16·1°, has a penetrating odour.

ω-*Trifluoro*-m-*cresol*, $CF_3 \cdot C_6H_4 \cdot OH$, prepared by diazotising trifluorotoluidinesulphate and decomposing the diazonium compound with

dilute sulphuric acid, forms a viscid liquid, b. p. 178·3°, which yields crystals, m. p. − 1·8°.

On diazotising o-phenetidine in hydrofluoric acid a mixture of o-fluorophenetole and ordinary phenetole is obtained.   o-*Fluorophenetole* has b. p. 171·4°, m. p. − 16 7°.   m-*Fluorophenetole*, prepared in a similar manner, is a colourless liquid, b. p. 171·4°/755 mm., $D_{16·4}$ 1·0716, n_D 1·4847.

p-*Fluorophenetole* cannot be separated from phenetole by distillation ; after fractional crystallisation the pure product had m. p. − 8·5°, b. p 172·8° 766 mm., $D_{18·9}$1·07148, n_D1·48257.   The product described by Valentiner and Schwarz (*Zeitsch. angew. Chem.*, 1898, 11, 441), b. p. 197°, as p-fluorophenetole is shown to be mainly p-chlorophenetole.

On nitration of p-fluorophenol, 4-*fluoro-2-nitrophenol* is obtained, crystallising in hexagonal prisms, m. p. 73·7° ; the *sodium* and *potassium* salts form long, red needles which explode when heated.

The   corresponding   4-*fluoro-2 nitrophenetole*   yields   colourless crystals, m. p. 33·7°.   4-*Fluoro-2 : 6 dinitrophenol* crystallises in very beautiful yellow prisms, m. p. 50·2°.

On nitration of m-fluorophenol, a *dinitro*-derivative is obtained in large, colourless, straw-like crystals becoming yellow on exposure to light, m. p. 72—74° ; the constitution has not been established.

p-*Difluorobenzene* prepared from p fluoroaniline is an oil, b. p. 88—89°, $D_{18·5}$ 1·1725, n_D 1·4422, m. p. − 23·7°.

On nitration 1 : 4-*difluoro-2-nitrobenzene* is obtained as a pale yellow oil, b. p. 103°/25 mm., m. p. − 11·7° ; it is very viscous at low temperatures.   The oil has $D_{17·2}$ 1·4671, n_D 1·5115.   E. F. A.

Chloronitrotoluenes with Reactive Chlorine.   WALTHER BORSCHE and ANNA FIEDLER (*Ber.*, 1913, 46, 2117—2131.   Compare A., i, 175).—In continuation of the earlier investigation which led to the isolation of pure 2-chloro-3 : 5-dinitrotoluene, the authors have turned their attention to the corresponding derivatives of p- and m-chlorotoluenes.   Their results indicate, among other facts, that pure 4-chloro-3 : 5-dinitrotoluene has not been previously obtained (compare Hönig, A., 1887, 1034).

The further nitration of 4-chloro-3-nitrotoluene by gradual addition to a cooled mixture of equal volumes of sulphuric acid and nitric acid (D 1·52) gives an impure reaction product from which by repeated crystallisation from alcohol pure 4-chloro-3 : 5-dinitrotoluene, needles, m. p. 115—116°, can be separated.   It reacts with ethyl sodiomalonate in warm ethereal solution, producing, after acidification, *ethyl 2 : 6 dinitro-p-tolylmalonate*, $C_6H_2Me(NO_2)_2 \cdot CH(CO_2Et)_2$, colourless crystals, m. p. 90°, which on heating with a mixture of acetic acid and a little diluted sulphuric acid passes into 2 : 6-*dinitro-p-tolylacetic acid*,

$$C_6H_2Me(NO_2)_2 \cdot CH_2 \cdot CO_2H,$$
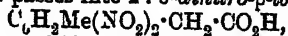
colourless needles, m. p. 241—242° (decomp.).   4-Chloro-3 : 5-dinitrotoluene also reacts with aniline, yielding 3 : 5-dinitro-4-anilinotoluene. The chlorodinitrotoluene can also be obtained in small quantity by the action of toluene-p-sulphonyl chloride on dinitro-p-cresol in the presence of diethylaniline.   In preparing the compound by the first method a

substance, m. p. 108°, possibly 4-chloro-2 : 5-dinitrotoluene, which does not react with aniline, is simultaneously produced.

The main product in the nitration of *m*-chlorotoluene by Reverdin and Crepieux's method (A., 1900, i, 638) is 3-chloro-4 : 6-dinitro toluene, m. p. 91°. It reacts in warm ethereal solution with ethyl sodioacetoacetate, producing *ethyl* 4 : 6-*dinitro*-m-*tolylacetoacetate*,

$$C_6H_2Me(NO_2)_2 \cdot CHAc \cdot CO_2Et,$$
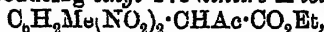
yellow tablets, m. p. 98°, which on warming with sulphuric acid undergoes scis-ion, yielding 4 : 6-*dinitro*-m-*tolylacetone*,

$$C_6H_2Me(NO_2)_2 \cdot CH \cdot CO \cdot CH_3,$$
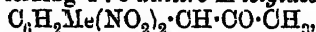
leaflets, m. p. 92°; also with ethyl sodiomalonate, it gives *ethyl* 4 : 6-*dinitro*-m-*tolylmalonate*, pale yellow crystals, m. p. 62°, which on heating with diluted sulphuric acid in acetic acid solution passes into 4 : 6-*dinitro*-m-*tolylacetic acid*, colourless needles, m. p. 176°; this substance when maintained at its m. p. loses carbon dioxide with production of 4 : 6-dinitro-1 : 3-xylene, m. p. 93—94°. *Ethyl* 4 : 6-*dinitro*-m-*tolylacetate*, colourless needles, m. p. 70°, is slowly converted by the action of sodium and more *m*-chlorodinitrotoluene in alcoholic solution at the ordinary temperature into *ethyl* 4 : 6 : 4' : 6'-*tetranitro-di*-m-*tolylacetate*, $CO_2Et \cdot CH_2[C_6H_2Me(NO_2)_2]_2$, needles, m. p. 159—160°, and also condenses at 180° with salicylaldehyde in the presence of a little piperidine, producing 3-o'p *dinitro*-m-*tolylcoumarin*,

$$\begin{matrix} C_6H_4\!-\!CH \\ O \quad -\!CO \end{matrix}\!\!\!>\!\!C\!-\!C_6H_2Me(NO_2)_2,$$ yellow needles, m. p. 240°, with a
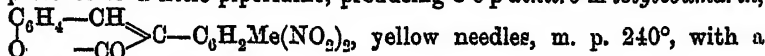
little 4 : 6-*dinitro-3-coumarino-2'-hydroxystilbene*,

$$\begin{matrix} C_6H_4\!-\!CH \\ O \quad\quad -\!CO \end{matrix}\!\!\!>\!\!C\!-\!C_6H_2(NO_2)_2 \cdot CH\!:\!CH \cdot C_6H_4 \cdot OH.$$
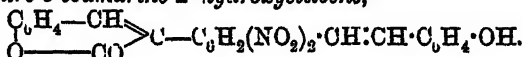
4 : 6-Dinitro-*m*-toluidine is obtainable by heating the corresponding chlorodinitrotoluene with alcoholic ammonia at 100°, and if the ammonia be replaced by aniline, *phenyl-*4 : 6-*dinitro*-m-*tolylamine*,

$$C_6H_2Me(NO_2)_2 \cdot NHPh,$$
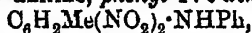
orange-coloured leaflets, m. p. 145°, is obtained. The former of these products readily condenses at 180—190° with benzaldehyde in the presence of piperidine with formation of 4 : 6-*dinitro-3-anilinostilbene*, $NHPh \cdot C_6H_2(NO_2)_2 \cdot CH\!:\!CHPh$, deep red leaflets, m. p. 182°. The chlorodinitrotoluene likewise condenses with piperidine when heated with the hydrochloride of the base and sodium acetate in alcoholic solution, giving 4 : 6-dinitro-3-piperidinotoluene, yellow rhombs, m. p. 116°; this can be further condensed with benzaldehyde, 4 : 6-*dinitro-3-piperidinostilbene*, yellowish-red crystals, m. p. 172°, being produced.

If the mother liquors from the crystallisation of 3-chloro-4 : 6-dinitrotoluene are treated with ethyl sodiomalonate or sodioacetoacetate, an unreactive isomeride, 3-*chloro*-2 : 4-*dinitrotoluene*, yellowish-white needles, m. p. 73°, remains unaffected ; its structure is indicated by its conversion through the corresponding *dinitrotolylhydrazine* (*hydrochloride*, yellow needles) by the action of ammonium hydroxide into 4-*nitro-5-methyl-1-hydroxy* 1 : 2 : 3-*benzotriazole*,

$$C_6H_2Me(NO_2)\!\!<\!\!\begin{matrix} \overbrace{\quad\quad}\!\!-N \\ N(OH) \end{matrix}\!\!\!>\!\!N,$$
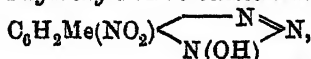
decomp. at 176° (compare Borsche and Rantscheff, A., 1911, i, 329).

2-Chloro-3 : 5-dinitrotoluene reacts with ethyl sodioacetoacetate in ethereal suspension with formation of *ethyl a-4 : 6-dinitro-o-tolylacetoacetate*, yellow needles, m. p. 79—80°, from which 4 : 6-*dinitro-o-tolylacetone*, pale yellow leaflets, m. p. 103—104°, can be obtained by hydrolysis with dilute sulphuric acid. In a similar manner, condensation with ethyl sodiomalonate yields *ethyl 4 : 6-dinitro-o-tolylmalonate*, yellow prisms, m. p. 87—88°, which on heating with diluted sulphuric acid in acetic acid solution is converted into 4 : 6-*dinitro-o-tolylacetic acid*, colourless needles, m. p. 202° (decomp.) ; this when heated readily loses a molecule of carbon dioxide with formation of 3 : 5-*dinitro-*1 : 2-*xylene*, m. p. 74—75°.   D. F. T.

Solubilities of the Rare Earth Salts of Bromonitrobenzenesulphonic Acid. S. H. KATZ and CHARLES JAMES (*J. Amer. Chem. Soc.*, 1913, **35**, 872—874).—1 : 4 : 2-Bromonitrobenzenesulphonic acid, prepared by sulphonation of bromonitrobenzene, forms nicely crystalline salts with lanthanum ($8H_2O$), cerium ($8H_2O$), yttrium ($10H_2O$), praseodymium ($8H_2O$), neodymium ($8H_2O$), samarium ($10H_2O$), europium ($10H_2O$), gadolinium ($10H_2O$), erbium ($12H_2O$), thulium ($12H_2O$), and ytterbium ($12H_2O$). The solubility of each salt was determined at 25°, and it is interesting that on plotting the solubilities against the atomic weight, salts containing the same amount of water of crystallisation fall on distinct portions of the curve.   D. F. T.

Nitration of Iodobenzene. ARNOLD F. HOLLEMAN (*Rec. Trav. chim.*, 1913, **32**, 134—139).—In a previous investigation of the nitration of iodobenzene (A., 1912, i, 87), the author has found that the quantity of ortho-isomeride formed is less than that obtained in the nitration of bromobenzene, whilst in the nitration of other aryl haloids, the quantity of this isomeride increases with the atomic weight of the halogen, and also that a greater amount of o-iodonitrobenzene is obtained at −30° than at 0°, although the amount of accessory product generally increases with increasing temperature of nitration.

[With A. F. H. LOBRY DE BRUYN and W. J. DE MOOY.]—The previous work has been repeated and a new source of error discovered due to the ready solubility of o-iodonitrobenzene in iodobenzene, in which p-iodonitrobenzene is practically insoluble. The iodobenzene is now added slowly to the nitric acid (D 1·482 for nitration at 0° and D 1·488 for nitration at −30°) with brisk stirring, smaller quantities of concentrated nitric acid being added from time to time if the mass becomes too viscous. Agitation is continued for two to three hours after completion of the addition of iodobenzene. The mass is then poured into water, filtered, dried, and distilled under diminished pressure. In this manner the determination of the point of solidification is greatly facilitated.

The authors are led to the conclusion that the iodobenzene does not differ from that of the other phenyl haloids. At −30°, 39·1% of the ortho- and 60·9% of the para-isomeride are obtained, whilst at 0° the figures are 41·1% ortho- and 58·7% para-isomeride.   H. W.

Some Diphenylpentanes and the Corresponding Dicyclo-hexylpentanes. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, **156**, 1951—1954. Compare this vol., i, 716; A., 1912, i, 617, 757).—The authors have already reduced various diphenylethanes, diphenylpropanes, and diphenylbutanes to the corresponding dicyclohexyl derivatives, and in order to test the general character of the hydrogenation still further, have now submitted three of the eighteen theoretically possible diphenylpentanes to similar treatment.

By catalytic treatment of β-phenylpropionic acid with thoria or iron oxide, $\alpha\epsilon$-*diphenylpentan-γ-one*, $CH_2Ph\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2Ph$, was first prepared, which, by contact with a not too active nickel at 180° in the presence of hydrogen, is converted smoothly into $\alpha\epsilon$-*diphenylpentane*, a fluorescent colourless liquid, b. p. 324° (corr.), D_0^9 0·9924, n_D^{19} 1·559. By hydrogenation under the influence of a very active nickel at 165°, this hydrocarbon is entirely reduced to $\alpha\epsilon$-*dicyclohexylpentane*, $C_6H_{11}\cdot[CH_2]_5\cdot C_6H_{11}$, a colourless liquid, b. p. 311° (corr.), D_0^9 0·8832, n_D^{21} 1·479, which resists the action of a cold mixture of nitric and sulphuric acids.

Methyl *iso*valerate reacts with magnesium phenyl bromide, yielding $\alpha\alpha$-*diphenyl-γ-methylbutanol*, $CHMe_2\cdot CH_2\cdot CPh_2\cdot OH$, which undergoes dehydration when distilled under the ordinary pressure, with production of $\alpha\alpha$-*diphenyl-γ-methyl-Δ^α-butene*, $CHMe_2\cdot CH:CPh_2$, a pale yellow liquid, b. p. 298—299° (corr.), D_0^{21} 0·9792, n_D^{21} 1·581. When submitted to the action of hydrogen under the influence of a sluggish nickel catalyst at 180°, the last-named hydrocarbon undergoes reduction to $\alpha\alpha$-*diphenyl-γ-methylbutane*, $CHMe_2\cdot CH_2\cdot CHPh_2$, a colourless, slightly fluorescent liquid, b. p. 297° (corr.), D_0^9 0·9756, n_D^{21} 1·551, which is still further reduced under the catalytic influence of a very active specimen of nickel at 160—165°, giving $\alpha\alpha$-*dicyclohexyl-γ-methylbutane*, $CHMe_2\cdot CH_2\cdot CH(C_6H_{11})_2$, a colourless liquid, b. p. 290—291° (corr.), D_0^9 0·9058, n_D^{21} 1·489.

Magnesium ethyl iodide reacts with *diphenylpropanone*,
$$CH_2Ph\cdot CO\cdot CH_2Ph,$$
which is obtainable by catalytic treatment of phenylacetic acid with iron oxide, producing *dibenzylethylcarbinol*, $CH_2Ph\cdot CEt(OH)\cdot CH_2Ph$; this passes on mere distillation under ordinary pressure into $\alpha\gamma$-*diphenyl-β-ethyl-Δ^α-propylene*, $CHPh:CEt\cdot CH_2Ph$, b. p. 306—307°, D_0^{21} 1·0159, n_D^{21} 1·589. By means of a sluggish nickel catalyst at 230° this can be hydrogenated to $\alpha\gamma$-*diphenyl β-ethylpropane*, $CH_2Ph\cdot CHEt\cdot CH_2Ph$, a colourless, fluorescent liquid, b. p. 304—305° (corr.), D_0^9 0·9855, n_D^{21} 1·553. When submitted to an active nickel catalyst below 180° it is reduced by hydrogen to $\alpha\gamma$-*dicyclohexyl-β-ethylpropane*,
$$C_6H_{11}\cdot CH_2\cdot CHEt\cdot CH_2\cdot C_6H_{11},$$
a colourless liquid, b. p. 296° (corr.), D_0^9 0·8966, n_D^{21} 1·843, which is not attacked by a cold mixture of sulphuric and nitric acids.
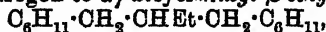
A comparison of the m. p.'s and b. p.'s of the diphenyl derivatives in which the two phenyl groups are connected by a normal chain of carbon atoms reveals the fact that whilst the latter increases steadily with an increasing number of linking atoms, the m. p.'s exhibit an undulating increase similar to that observed with the dicarboxylic acids. It is also noteworthy that whilst all the diphenyl hydro-

carbons are fluorescent, this property is most marked in those having the two phenyl radicles coupled by a normal chain of methylene linkings ; the dicyclohexyl derivatives possess no fluorescence.

<div align="right">D. F. T.</div>

The Constitution of Naphthalene. EUGEN BAMBERGER (*Ber.*, 1913, **46**, 1899—1903).—Since his earlier publications (a list of which is appended to the paper), the author's views on this subject have undergone modifications. Although he still regards the symmetry of naphthalene as highly probable, he realises that there has been no final proof. The formula suggested by Willstätter and Waser (A., 1912, i, 17) fails to express the reduction of naphthalene and its derivatives, which possess no true aromatic character, to aromatic compounds. This peculiar behaviour of naphthalene derivatives can be explained by other symmetrical formulæ in addition to the author's, provided that they do not include a true benzene ring, but the author repeats his earlier statement (*J. pr. Chem.*, 1890, **42**, [2], 205) that it is not possible to represent completely the various chemical phenomena presented by naphthalene derivatives in any one formula of the usual type.

<div align="right">D. F. T.</div>

10-Bromophenanthrene-3- or -6-sulphonic Acid. HÅKAN SANDQVIST (*Annalen*, 1913, **398**, 125—137).—By heating with 96—97% sulphuric acid on the water-bath and finally at 150—155°, 10-bromophenanthrene is converted into an acid which is proved to be 10-bromophenanthrene-3- or -6-sulphonic acid, and is isolated as the potassium salt. The free acid, prepared from the chloride and water at 130—135°, is an almost colourless, crystalline powder. It contains $3H_2O$, and has m. p. 162—164·5° (anhydrous, 200—201·5°). A 10% aqueous solution of the acid, which is as clear and viscous as water, becomes syrupy by the addition of a little dilute hydrochloric, nitric, or sulphuric acid, and finally deposits crystals of the acid by further addition of the mineral acid. The following salts are described, the figures in brackets denoting the weight of anhydrous salt dissolved by 100 grams of water at 19·5°: *ammonium* salt containing H_2O (0·327), *sodium* salt containing $1\frac{1}{2}H_2O$ (0·142), *potassium* salt with H_2O (0·163), *calcium* salt with $4H_2O$, *barium* salt with $2\frac{1}{2}H_2O$, *cupric* salt with $4H_2O$; the last three salts are quantitatively insoluble. The *methyl* ester, m. p. 172·5—173°, *ethyl* ester, m. p. 173—173·3°, *chloride*, $C_{14}H_8O_2ClBrS$, m. p. 184·5—185°, *sulphonamide*, m. p. 280—281°, and dimorphous *anilide*, m. p. 185·5—186° or 193°, are described.

By oxidation with chromic acid in boiling glacial acetic acid, 10-bromophenanthrene-3-(or 6-)-sulphonyl chloride and methyl 10-bromophenanthrene-3-(or 6-)-sulphonate respectively yield substances, m. p. 230—238° and 230—233°, which are apparently phenanthraquinone-3-sulphonyl chloride, m. p. 232—234°, and methyl phenanthraquinone-3-sulphonate, m. p. 234°, respectively.

Potassium or methyl 10-bromophenanthrene-3-(or 6-)-sulphonate are not attacked by reducing agents in acid or neutral media ; concentrated aqueous ammonia and zinc dust on the water-bath reduce the potassium salt, yielding phenanthrene-3-sulphonic acid.

<div align="right">C. S.</div>

Photochemical Transformations of Acenaphthylene. II. KARL DZIEWOŃSKI and C. PASCHALSKI (*Ber.*, 1913, **46**, 1986 -1992. Compare A., 1912, i, 844).—The two hydrocarbons, m. p. 306—367° and m. p. 232—234°, which are obtained by the action of sunlight on acenaphthylene are *cis-trans*-isomerides and may be represented by the formulæ :
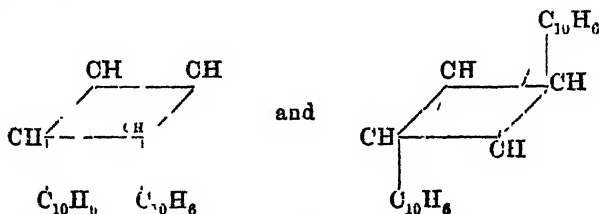
The compounds are formed in different quantities according to the nature and concentration of the solution and to the intensity of the light. They both yield naphthalic anhydride on oxidation and are partly converted into the parent substance in the molten state, but they form entirely different picrates and bromo compounds. Although it cannot be said which of the isomerides is the labile modification, it is proposed to call the higher and the lower melting forms α- and β-*heptacyclene* respectively.

The former is the chief product when a benzene solution of acenaphthylene is illuminated, but the β-form predominates when petroleum is used as the solvent. β-*Heptacyclene*, $C_{24}H_{16}$, forms large, monoclinic prisms or tablets, $a : b : c = 0.7223 : 1 : 0.9527$, $\beta = 119°6'$, and is readily soluble in benzene. Both substances yield new, complex hydrocarbons when kept in the molten state for some time, but, when the mass is quickly cooled, some acenaphthylene is obtained and this is probably the parent of the new compounds, for it is unstable above 110°.

α-Heptacyclene combines with two molecules of picric acid in ethylene dibromide solution, yielding the *picrate*,

$$C_{24}H_{16}, 2C_6H_2(NO_2)_3 \cdot OH,$$
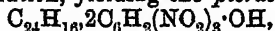
in orange needles, m. p. 225—227°, which are decomposed even by solvents, whereas β-heptacyclene forms a stable *picrate*,

$$C_{24}H_{16}, C_6H_2(NO_2)_3 \cdot OH,$$
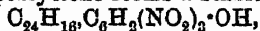
in carmine-red needles, m. p. 215—216°. The α-hydrocarbon reacts very sluggishly with bromine in the cold, but the β-form absorbs bromine at once. J. C. W.

Perylene and Its Derivatives. II. RICHARD WEITZENBÖCK and CHRISTIAN SEER [with A. VON BARTSCH] (*Ber.*, 1913, **46**, 1994—2000. Compare A., 1910, i, 616).—Attempts have been made to improve the yield of perylene or its derivatives. The best result was obtained by the condensation of 4 : 4'-dicyano-1 : 1'-dinaphthyl to 3 : 10-dicyanoperylene.

From bromonaphthalene and aluminium chloride, a 4% yield of perylene was obtained at 140°, but at 30—35° the product was 2 : 2'-dinaphthyl, which was probably formed by the rearrangement of 1 : 1'-dinaphthyl. β-Dinaphthylene oxide (Eckstein, A., 1905, i, 885)

was also heated with aluminium chloride, when alkali extracted from the product, 1-*hydroxyperylene* (I). This forms long, slender, yellow needles, m. p. 197°, which give yellow solutions with green fluorescence, and yield a *benzoate*, $C_{27}H_{16}O_2$, in slender, lemon-yellow needles, m. p. 170—170·5°, and a *methyl ether* in yellow nodules, m. p. 111°. The residue from the extraction with alkali contained 1 : 12-*furoperylene* (II), which forms a reddish-brown powder, and gives dark red solutions with yellowish-brown fluorescence.
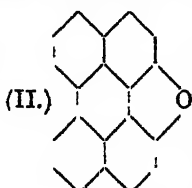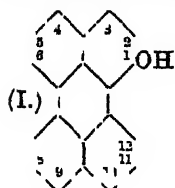
3 : 10-*Dicyanoperylene*, $C_{22}H_{10}N_2$, was obtained in good yield by the condensation of 4 : 4′-dicyano-1 : 1′-dinaphthyl (Seer and Scholl, this vol., i, 734) in brown, microscopic needles, m. p. 368—369°. It is sparingly soluble in acetic acid or xylene with intense green fluorescence, and yields 3 : 10-*perylenedicarboxylic acid*, $C_{22}H_{12}O_4$, when heated with alcoholic sodium hydroxide in a sealed tube. The acid forms reddish-brown, microscopic needles, and the solutions in alkalis are yellow with intense green fluorescence. The *ethyl* ester, $C_{26}H_{20}O_4$, forms brick-red leaflets, m. p. 247—248°.

4 : 4′-Di-iodo-1 : 1′-dinaphthyl (Willgerodt and Schlösser, A., 1900, i, 282) was prepared from naphthidine by treating the diazonium salt with potassium iodide. When heated with aluminium chloride, extensive decomposition took place.   J. C. W.

Degradation of Decacyclene [Trinaphthylenebenzene]. KARL DZIEWONSKI [with J. PODGÓRSKA and A. MIKLASZEWSKI] (*Ber.*, 1913, 46, 2156—2162).—When finely powdered decacyclene (A., 1903, i, 431) is heated for some hours with sodium dichromate and 30% sulphuric acid, it is broken down into *tribenzoylenebenzenetricarboxylic acid*, $C_6\left(<^{CO}_{C_6H_3 \cdot CO_2H}\right)_3$, which is formed in good quantity, as a brownish-red, voluminous, microcrystalline mass, m. p. above 360°. The acid gives blood-red solutions in alkalis, and forms, by precipitation, a brown *silver* salt, $C_{30}H_9O_9Ag_3$, and a reddish-brown *barium* salt, $(C_{30}H_9O_9)_2Ba_3$. When the calcium salt is distilled with lime, a sublimate of large, orange-yellow needles of tribenzoylenebenzene (truxenequinone),
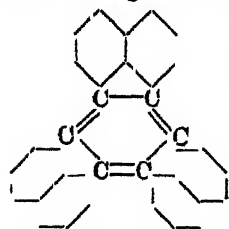
$$C_6\left(<^{CO}_{C_6H_4}\right)_3$$
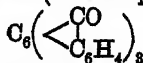
(Michael, A., 1906, i, 518) is formed. On heating the acid for three or four hours with the theoretical amount of potassium permanganate in a large excess of 2% sodium hydroxide, it is oxidised to dicarboxyphenylglyoxylic acid, $C_6H_3(CO_2H)_2 \cdot CO \cdot CO_2H$ (Graebe and Bossel, A., 1896, i, 436), and an acidic by-product, but complete oxidation with an excess of permanganate results in the formation of hemimellitic acid (Graebe and Leonhardt, A., 1896, i, 437). The constitution of decacyclene is therefore represented by the annexed formula.   J. C. W.

Strain Laws of Ring Systems. Oscar Hinsberg (*J. pr. Chem.*, 1913, **88**, [ii], 58—60).—It has been shown previously (A., 1902, i, 238; 1904, i, 200) from a comparison of the stability of various azines and acridine derivatives, that the strain in tertiary ring systems, composed of 6-membered rings arranged in linear order, increases rapidly with the complexity of the molecule, so that a system containing five conjugated rings is either very unstable or incapable of existence.

The author refers to the unsuccessful attempts of W. A. and M. Mills (T., 1912, **101**, 2194) to prepare dinaphanthracene by the oxidation of its di- and tetra-hydro-derivatives in support of this view, and points out that their work renders it probable that the strain laws, developed by him for ring-systems containing carbon and nitrogen, are also applicable to systems composed wholly of carbon rings.

F. B.

Metaquinonoids. II. Otto Stark and O. Garben (*Ber.*, 1913, **46**, 2252—2259).—The possibility that the yellow hydrocarbon, obtained previously (this vol., i, 362) by the removal of halogen from tetraphenyl-*m*-xylylene dichloride, is a triarylmethyl derivative and not a true metaquinonoid compound, is excluded on account of the comparatively great stability of the hydrocarbon towards air and oxygen, and its inability to form additive compounds with ether, ethyl acetate, benzene, alcohol, acetic acid, and acetic anhydride.

A benzene solution of the hydrocarbon, after being exposed to air for eight weeks, and occasionally treated with oxygen during this time, deposited a white, amorphous *oxide*,
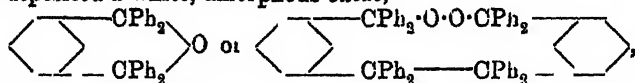
which is insoluble in all the usual solvents with the exception of hot nitrobenzene, and when heated becomes discoloured and slowly decomposes at 200°, the decomposition being complete at 250°.

On treatment with hydrogen chloride in benzene, it yields an additive *compound* formed by the union of four molecules of the hydrocarbon with one of hydrogen chloride. This compound crystallises in white needles, m. p. 286—287° (decomp.), with previous darkening at 275°, and is considered to have the following constitution :

$$CPh_2 \cdot C_6H_4 \cdot CPh_2 \cdot CPh_2 \cdot C_6H_4 \cdot CHPh_2$$
$$CPh_2 \cdot C_6H_4 \cdot CPh_2 \cdot CPh_2 \cdot C_6H_4 \cdot CPh_2Cl$$
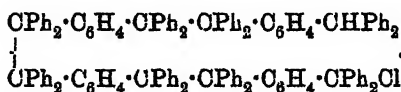
It dissolves in boiling benzene, yielding deep yellow solutions, but the molecular weight in these solutions is only half that corresponding with the above formula. The authors interpret these results as indicating that the substance undergoes dissociation, at the position shown by the dotted line, into two triarylmethyl residues.

During the preparation of the hydrocarbon, an isomeride was obtained (*loc. cit.*) which had a higher m. p., and was supposed to be identical with Thiele's tetraphenyl-*p*-xylylene. The identity of the two compounds has now been fully established. The simultaneous

formation of the para-quinonoid hydrocarbon is due, however, not to a wandering of the groups in the meta-compound as was imagined previously, but to the original methyl *iso*phthalate, from which the hydrocarbon was prepared, being contaminated by considerable quantities of methyl terephthalate.

The *diethyl ether* of tetraphenyl-*m*-xylylene glycol, prepared by boiling the corresponding chloride with alcohol, has m. p. 116—117°; the *methyl ether*, m. p. 103—104°. The *diacetyl* derivative, prepared from the glycol and acetic anhydride, has m. p. 90—91 5°.

Tetraphenyl-*p*-xylylene glycol crystallises from glacial acetic acid in well developed prisms, m. p. 168—169°, containing the solvent (1 mol.), which is removed by heating the crystals under diminished pressure at 130—140°; the glycol then has m. p. 171—171·5°. The *diacetyl* derivative sinters at 198°, m. p. 203—204°.

Tetraphenyl-p-*xylylene dichloride*, prepared by passing hydrogen chloride into an acetic acid solution of the glycol, crystallises in slender, flat prisms, m. p. 239—240°, with previous sintering and darkening.   F. B.

Nitro-derivatives of *p*-Phenetidine.   FRÉDÉRIC REVERDIN and LUDWICK FURSTENBERG (*Arch. Sci. phys. nat.*, 1913, 35, 594—605; *Bull. Soc. chim.*, 1913, [iv], 13, 671—681).—The present work has been undertaken in continuation of the experiments of Reverdin and de Luc (A., 1909. i, 377, 913) on the nitration of *p*-anisidine.   The initial materials in the various experiments are aceto-*p*-phenetidide, toluenesulpho-*p*-phenetidide, o-*nitrotoluenesulpho*-p-*phenetidide*,

OEt·C₆H₄·NH·SO₂·C₆H₃Me·NO₂,
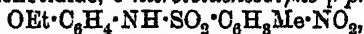
needles, m. p. 128°, and m-*nitrophenylsulpho-p-phenetidide*.

OEt·C₆H₄·NH·SO₂·C₆H₄·NO₂,
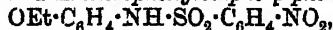
prismatic needles, m. p. 129—130°, the two latter substances being obtained by the action of the corresponding chlorides on an alcoholic solution of *p*-phenetidine in the presence of sodium acetate.

2 : 3-Dinitro-*p*-phenetidine (compare Wender, A., 1890, 751) is formed by the action of concentrated sulphuric acid on 2 : 3-*dinitro-p-toluene-sulphophenetidide*, white needles, m. p. 163°, obtained by the addition of nitric acid (D 1·52) to a solution of toluenesulpho *p*-phenetidide in glacial acetic acid.

3 : 5-*Dinitro-o-nitrotoluenesulpho-p-phenetidide*,

OEt·C₆H₂(NO₂)₂·NH·SO₂·C₆H₃Me·NO₂,
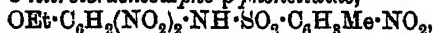
slender needles, m. p. 163°, is prepared by the action of nitric acid (D 1·4) on a solution of *o*-nitrotoluenesulpho-*p*-phenetidide in glacial acetic acid.   Energetic treatment with concentrated sulphuric acid converts it into 3 : 5-dinitro-*p*-aminophenol, m. p. 230°, from which the position of the nitro-groups is ascertained, whilst a milder treatment leads to the formation of 3 : 5-*dinitro*-p-*phenetidine*, red leaflets, m. p. 138—139°.   The same base can be obtained by the saponification of the product formed when 3-nitrotoluenesulpho-*p*-phenetidide is nitrated in acetic acid solution.

When phenacetine is nitrated in sulphuric acid solution under definite conditions, 2 : 6-dinitro-*p*-phenacetine, OEt·C₆H₂(NO₂)₂·NHAc, white needles, m. p. 148°, is formed, which, when hydrolysed by dilute

sulphuric acid, is converted into 2:6-*dinitro*-p-*phenetidine*, yellow leaflets, m. p. 172°. The constitution of the base follows from the identity with the product obtained by the ethylation of *isopicramic* acid.

Unsuccessful attempts have been made to prepare 2:5-dinitro-*p*-phenetidine by the nitration of phenacetine or of *m*-nitrobenzene-sulpho-*p*-phenetidide. In the latter case, the main product of the change was a 2:3-dinitro-derivative, m. p. 178°, which, on hydrolysis, yielded 2:3-dinitro-*p*-phenetidine, smaller quantities of a 3:5-dinitro-derivative being also formed

2:3:5-*Trinitrotoluenesulpho*-p-*phenetidide*, white needles, m. p. 217°, is prepared by nitrating 2:3-dinitrotoluenesulpho-*p*-phenetidide, and, when acted on by sulphuric acid, yields 2:3:5-*trinitro*-p-*phenetidine*, fine red needles with green reflex, m. p. 126—127°. The constitution of this substance is deduced from its analogy with the trinitro-*p*-anisidine obtained by Reverdin (A., 1910, i, 470) in which the nitro-groups are in the 2:3:5-positions, that in position 2 being mobile (compare Meldola and Kuntzen, T., 1910, 97, 444). This is established by converting it into dinitroguaiacol, dinitrocatechol, and dinitroveratrole of known constitution.

2:3:5-*Trinitroaceto*-p-*phenetidide*, OEt·$C_6H(NO_2)_3$·NHAc, white needles, m. p. about 245°, is obtained by the action of acetic anhydride and a trace of concentrated sulphuric acid on the free amine.

The following derivatives have been prepared by the replacement of the mobile nitro-group of 2:3:5-trinitro-*p*-phenetidine; 3:5-*dinitro-2-anilino*-p-*phenetidine*, OEt·$C_6H(NO_2)_2(NH_2)$·NHPh, brown leaflets, m. p. 151—152°; 3:5-*dinitro-2-methylamino*-p-*phenetidine*,

$$OEt·C_6H(NO_2)_2(NH_2)·NHMe,$$
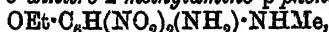
red needles, m. p. 166—167°; 3:5-*dinitro-2-dimethylamino*-p-*henetidine*, OEt·$C_6H(NO_2)_2(NH_2)$·NMe₂, m. p. 119—120°; 3:5-*dinitro-2 phenoxy*-p-*phenetidine*, OEt·$C_6H(OPh)(NO_2)_2$·NH₂, red needles, m. p. 185—186°; 3:5-*dinitro-2-amino*-p *phenetidine*, OEt·$C_6H(NO_2)_2(NH_2)_2$, m. p. 250°; 3:5-*dinitro-2-piperidino*-p-*phenetidine*,

$$OEt·C_6H(NO_2)_2(NH_2)·C_5NH_{10},$$
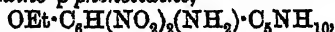
red leaflets, m. p. 143—144°.

2:5-*Dinitro-1-ethoxy-3:4-quinonediazide* (annexed formula: compare

Meldola and Reverdin, T., 1910, 97, 1204) is formed by the addition of sodium nitrite to a solution of 2:3:5-dinitro-*p*-phenetidine in sulphuric acid. It separates from acetic acid in orange prisms, m. p. 186°.
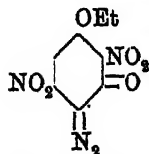
3:5-*Dinitro-2-hydroxy-p-phenetidine*, brown needles or blackish crystals with green metallic reflex, m. p. 166—167°, is prepared by boiling a solution of 2:3:5-trinitro-*p*-phenetidine in acetone with an alcoholic solution of sodium acetate. When the amino-group is removed in the usual manner, 3:5-*dinitro-2-hydroxyphenetole*, yellow leaflets, m. p. 155°, is obtained, the *barium* and *silver* salts of which were also examined. The latter, when treated with an alcoholic solution of ethyl iodide, yields slightly impure 3:5-dinitro-1:2-diethoxybenzene, m. p. 90—91°, probably identical with the product described by Blanksma (A., 1905, i, 431) to which the m. p. 94—95° is now assigned. **H. W.**

The Molecular Rearrangement of Triphenylmethylhydroxylamine. JULIUS STIEGLITZ and PAUL N. LEECH (*Ber.*, 1913, **46**, 2147—2151).—In accordance with Stieglitz's views as to the molecular rearrangement of bromoamides, hydroxamic acids, etc. (A., 1897, i, 43), which regard the Beckmann rearrangement with an oxime to occur by the steps

$$CR_2 \cdot N \cdot OH \xrightarrow{HCl} CR_2Cl \cdot NH \cdot OH \xrightarrow{H_2O} CR_2Cl \cdot N: \longrightarrow CRCl:NR,$$

it is found that triphenylmethylhydroxylamine, $CPh_3 \cdot NH \cdot OH$, which in constitution closely resembles the first class of product in the above series of changes, when treated in ethereal solution with phosphorus pentachloride is converted into benzophenoneanil, $CPh_2:NPh$, m. p. 111—112°. The above course of the rearrangement is thus confirmed.

<div align="right">D. F. T.</div>

The Molecular Rearrangement of Triphenylmethylbromoamine. JULIUS STIEGLITZ and ISABELLE VOSBURGH (*Ber.*, 1913, **46**, 2151—2156).—In an endeavour to decide which of the tautomeric forms $R \cdot CO \cdot NMX$ and $R \cdot C(OM):NX$ (M = metal, X = halogen) of the metallic salts of the halogenamides is to be regarded as the intermediate stage in the production of amines from halogen-amides by Hofmann's rearrangement, the authors have prepared and examined triphenylmethylbromoamine, $CPh_3 \cdot NHBr$, with which the possibility of tautomerism is excluded. By the action of alkali, the elements of hydrogen bromide are eliminated from this substance with formation of benzophenoneanil. The series of changes must therefore be $CPh_3 \cdot NHBr \longrightarrow CPh_3 \cdot NMBr \longrightarrow CPh_3 \cdot N: \longrightarrow CPh_2:NPh$. The former of the alternative structures thus receives support without excluding the possibility of the second formula being the correct one for the structure involved.

Triphenylmethylbromoamine, colourless crystals, m. p. 63°, was obtained by the action of bromine on triphenylmethylamine in chloroform solution in the presence of sodium hydroxide solution. By heating with soda-lime at 100—120°, or with a hot methyl alcoholic solution of sodium methoxide, it is converted into benzophenoneanil, m. p. 111—112°.

When heated to its m. p., triphenylmethyldichloroamine rapidly loses chlorine with the formation of benzophenoneanil with a little chlorobenzophenoneanil.

<div align="right">D. F. T.</div>

Oxidation of Organic Developers with Silver Salts. *p*-Aminophenol and Metol. FRITZ KROPF (*J. pr. Chem.*, 1913, [ii], **88**, 73—77).—On the addition of silver nitrate to an aqueous solution of *p*-aminophenol or *p*-methylaminophenol, the liquid acquires a bluish-violet colour and benzoquinone is produced.

In ammoniacal solution a blue coloration is produced, but no definite compound could be isolated from the reaction product.

When dissolved in aqueous sodium hydroxide and treated with silver bromide, *p*-aminophenol yields a *substance* which crystallises in brown leaflets having a metallic glance, m. p. 194° (not sharp), and gives a dark blue coloration on treatment with phenol and ammonia.

The addition of silver bromide to a solution of *p*-aminophenol in aqueous sodium hydroxide and in the presence of potassium meta-bisulphite results in the formation of a small amount of a white substance, which is probably a sulphonic acid ; under similar conditions metol yields a strongly green fluorescent solution, but no definite compound could be isolated.

The amount of silver reduced in the above reactions, and also the amount of sulphite which disappears, depends on the conditions under which the reduction is carried out. F. B.

Nitration of Anisole to Trinitroanisole. ALFRED L. BROAD-BENT and FIN SPARRE (*Eighth Inter. Cong. App. Chem.*, 1912, **4**, 15—17).—No experimental details of the preparation of 2 : 4 : 6-tri-nitroanisole from anisole appear to have been published ; the literature contains merely statements that the nitration is possible.

After considerable difficulties, the authors have evolved the follow-ing details which permit a yield of 85% of that theoretically expected from the anisole taken.

A mixture of 130 grams of nitric acid (D 1·52) with 220 grams of sulphuric acid (D 1·84), which is mechanically agitated by a stirrer, is cooled to −5° by immersion in a freezing mixture of ice and salt whilst 30 grams of anisole are added in small drops. The addition should occupy two to three hours, and the temperature of the mixture should never reach 0°. After all the anisole has been introduced, the temperature is raised to 65—70° for twenty minutes with continued stirring, and the mixture is then poured into water. After washing with warm water and dilute sodium carbonate solution successively, with subsequent drying, the product has m. p. 64—65°, D^{20} 1·408, and is slowly hydrolysed by water to methyl alcohol and picric acid.

D. F. T.

Hydrolysis of Trinitroanisole by Alkalis and Water. WALTER E. MASLAND and FIN SPARRE (*Eighth Inter. Cong App. Chem.*, 1912, **4**, 77) —Pure trinitroanisole is hydrolysed fairly rapidly by hot solutions of the alkali carbonates and slowly by hot water ; the action of each of these in the cold is much more feeble. Picric acid is produced in each case. D. F. T.

Action of Nitric Acid on Halogen Derivatives of *o* Alkyl-phenols. II Nitric Acid Derivatives of 3 : 4 : 5- and 3 : 5 : 6-Tribromo-*o*-cresols. THEODOR ZINCKE and NELSON W. JANNEY (*Annalen*, 1913, **398**, 343—353).—3 : 4 : 5- and 3 : 5 : 6-Tribromo-*o*-cresols react with nitric acid in the sense of the equation : $C_7H_5OBr_3 + 2HNO_3 = C_7H_5O_6N_2Br_3 + H_2O$, but the two products exhibit quite different behaviour. 3 : 4 : 5-Tribromo-*o*-cresol and nitric acid, D 1·48, yield by keeping 3 : 4 : 5 *tribromo*-o *cresol nitroquinitrol*,

$$NO_2 \cdot O \cdot C(OH) \underset{OBr(NO_2) \cdot CBr}{\overset{OMe \underline{\qquad} CH}{<}} > CBr,$$
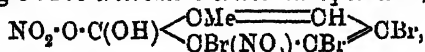
m. p. 126° (decomp.), colourless needles, which is not reconverted into the tribromo-*o*-cresol by reduction, yields tribromo-*p*-toluquinone by warming with concentrated sulphuric acid, and by boiling with

toluene, glacial acetic acid, or tetrachloroethane is converted by loss of nitrosyl bromide into 4 : 5-*dibromo-o-toluquinone* 2-*nitrate*,

$$NO_2 \cdot O \cdot C(OH) < ^{CMe:CH}_{CO-CBr} > CBr,$$
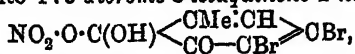
m. p. 173° (decomp.), pale yellow prisms. The latter is stable, dissolves in alkalis, and is reduced by stannous chloride, hydrochloric acid, and a little alcohol, to 4 : 5-*dibromo*-2 : 3-*dihydroxytoluene*, m. p. 104°, colourless needles, which forms a *diacetyl* derivative, m. p. 137—138°, and is oxidised by nitric acid, D 1·15, to 4 : 5-*dibromo-o-toluquinone*, $C_7H_4O_2Br_2$, m. p. 96—98°, dark red, crystalline powder.

3 : 5 : 6-Tribromo-*o*-cresol and nitric acid, D 1·48, at 0° yield 3 : 5 : 6-*tribromo-o-cresolnitroquinitrol*, $NO_2 \cdot O \cdot C(OH) < ^{CBr=CH}_{CMe(NO_2) \cdot CBr} > CBr,$
m. p. 96° (decomp.), faintly yellow leaflets or needles, which regenerates the tribromo-*o*-cresol by reduction with stannous chloride solution after being initially heated with glacial acetic acid for a short time.   C. S.

Bromo-derivatives of *o*-Cresol. NELSON W. JANNEY (*Annalen*, 1913, **398**, 354—372).—The author describes the preparation of some of the unknown brominated *o* cresols; usually the constitutions are determined by converting the substance ultimately into a quinone of the ortho- or of the para series.

4-*Bromo-o-cresol*, m. p. 80°, broad needles, prepared from diazotised 4-bromo-*o*-toluidine in the usual manner, forms a *benzoate*, m. p. 41°, and is converted by nitric acid, D 1·4, in glacial acetic acid into a *nitro-* and a *dinitro*-derivative, the latter, m. p. 169°, crystallising in yellow prisms.

3 : 4-*Dibromo-o-cresol*, m. p. 94—95°, colourless needles, is obtained by brominating 4-bromo-*o*-cresol in chloroform in the presence of a little iron. It forms an *acetate*, m. p. 49°, is converted by nitric acid, D 1·52, in glacial acetic acid into the preceding bromo-dinitro-*o*-cresol, and yields 3 : 4-dibromo-5-nitro *o*-cresol (see below) by treating its solution in glacial acetic acid with powdered sodium nitrite. 3 : 6-*Dibromo-o-cresol*, m. p. 38° (*benzoate*, m. p. 104°, white needles), is prepared in a similar manner from 6-bromo-*o*-cresol. Its constitution follows from the fact that it yields only oily products by treatment with sodium nitrite and acetic acid; were it 5 : 6-dibromo-*o*-cresol, it must have yielded 5 : 6-dibromo-3-nitro-*o*-cresol identical with that obtained from 3 : 5 : 6-tribromo-*o*-cresol (see below).

3 : 5-Dibromo-*o*-cresol is already known. By treatment with sodium nitrite and acetic acid at 12—15°, it is converted into 5-bromo-3-nitro-*o*-cresol, by the reduction of which 5-bromo-3-amino-*o*-cresol (*diacetyl* derivative, m. p. 203°) is obtained. The hydrochloride of the last substance, dissolved in glacial acetic and concentrated hydrochloric acids, is converted by moist chlorine into the *diketo-chloride*, $CClBr < ^{CCl:CMe}_{CCl_2-CO} > CO$, m. p. 80°, stout, yellow prisms, by the reduction of which by stannous chloride 4 : 6-*dichloro-5-bromo*-2 : 3-*dihydroxytoluene*, m. p. 186°, colourless needles (*diacetate*, m. p. 176—177°), is obtained. By oxidation with nitric acid, D 1·4, the last compound is

converted into 4 : 6-*dichloro*-5-*bromo*-o-*toluquinone*, m. p. 121—122°, red, crystalline powder.

By treatment with nitric acid, D 1·4, and glacial acetic acid, 3 : 5-dibromo-o cresol yields Auwers' 3-bromo-5-nitro-o-cresol, and finally 3 : 5-dinitro-o-cresol. By reduction with alcohol and stannous chloride, the former is converted into 3-*bromo*-5-*amino*-o-*cresol*, m. p. 146°, stout prisms (*acetyl* derivative, m. p. 152°; *diacetyl* derivative, m. p. 167°), from the *hydrochloride* of which 3-bromo-p-toluquinone is obtained by oxidation with potassium dichromate and dilute sulphuric acid.

3 : 4 : 5-Tribromo-o-cresol, m. p. 89° (not 79°, as stated in the literature), which is only occasionally obtained pure by the bromination of o-cresol, is prepared in 90—95% yield by the action of bromine and iron on 4-bromo-o-cresol in cold chloroform. It is most conveniently obtained by treating a solution of 3 : 5-dibromo-o-cresol in glacial acetic acid with 10% calcium hypobromite, and warming the resulting *keto-bromide*. $C_7H_6OBr_2$, m. p. 110° (decomp.), yellow prisms, with concentrated sulphuric acid. The action of sodium nitrite and glacial acetic acid on 3 : 4 : 5-tribromo-o-cresol yields Zincke and Hedenström's 3 : 4-dibromo-5-nitro-o-cresol, which by successive reduction, conversion into the diketo-chloride, and reduction is converted into 3 : 6-*dichloro*-4-*bromo*-p-*toluquinol*,

$$\text{OH·C} \underset{\text{CCl·CBr}}{\overset{\text{CMe:CCl}}{<}} \!\!\!\!> \text{C·OH,}$$
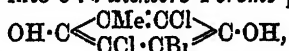
m. p. 200—201°, white prisms or needles (*diacetate*, m. p. 226—227°). By oxidation with nitric acid, the quinol is converted into 3 : 6-*dichloro*-4-*bromo*-p-*toluquinone*, m. p. 233°, yellow, hexagonal leaflets. The production of a para-quinone proves the constitution of 3 : 4 : 5-tribromo-o-cresol and also of 3 : 4-dibromo-o-cresol.

3 : 5 : 6-*Tribromo*-o-*cresol*, m. p. 91°, prismatic needles (*acetate*, m. p. 76—77°), is prepared from 6-bromo-o-cresol in a similar manner as 3 : 4 - 5-tribromo-o-cresol from 4-bromo-o-cresol. By treatment with sodium nitrite and glacial acetic acid at 12—15°, it yields 5 : 6-*dibromo*-3-*nitro*-o-*cresol*, m. p. 100°, pale yellow needles (*acetate*, m. p. 74°), from which 4 : 6-dichloro-5-bromo-2 : 3-dihydroxytoluene and 4 : 6-dichloro-5-bromo-o-toluquinone, identical with the corresponding substances obtained from 3 : 5-dibromo-o-cresol, are obtained by reduction and treatment of the keto-chloride in the usual manner.　C. S.

[1-Methyl*cyclo*pentane-1-carboxylic Acid.] I. PETROV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 644).—For this acid the author finds the constants, b. p. 216—217°, D_0^0 1·0386 (compare Tschitschibabin, this vol., i, 467).　T. H. P.

Four Different Anhydrides of Dibenzylacetic Acid. The Catalytic Action of Metaphosphoric Acid on Acid Chlorides. HERMANN LEUCHS, JOHANNES WUTKE, and ERICH GIESELER (*Ber.*, 1913, 46, 2200—2215).—According to Staudinger and Ott (A., 1908, i, 602) the action of thionyl chloride on malonic acids results primarily in the formation of the semi-chlorides which may subsequently part with carbon dioxide to give the acetyl chlorides, or lose hydrogen chloride

to form malonic anhydrides and finally ketens, as in the following case :

$$CHMe_2 \cdot COCl \longleftarrow CMe_2 \!\!<^{COCl}_{CO_2H} \longrightarrow CMe_2 \!\!<^{CO}_{CO}\!\!>O \longrightarrow CMe_2 \!\!:\!\! CO.$$
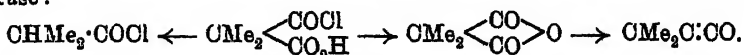
In the case of dibenzylmalonic acid, the chief product is dibenzylacetyl chloride, but a by-product is also formed which is a simple polymeride of dibenzylketen and is shown to be tetrabenzyl*cyclo*butan-1 : 3-dione,

$$C(CH_2Pn)_2 \!\!<^{CO}_{CO}\!\!> C(CH_2Ph)_2$$ That its formation is due to the inter-

vention of dibenzylketen is assumed from the fact that the substance could not be obtained from dibenzylacetic acid or dibenzylacetyl chloride.

In order to moderate the action of thionyl chloride, with the hope of obtaining the semi-chloride of dibenzylmalonic acid, the reagent was diluted with ether, but it was found that the action was too moderate, the product being the ordinary anhydride of dibenzylacetic acid, $[CH(CH_2Ph)_2 \cdot CO]_2O$.

Attempts were made to prepare the *cyclo*butane derivative from dibenzylacetyl chloride. When this substance was heated at 250°, it gradually parted with hydrogen chloride, but the product was a third anhydride, m. p. 145°. In some experiments on the preparation of the chloride, it was found that, unless an excess of phosphorus penta-chloride was employed, the metaphosphoric acid, or some similar product from the phosphoryl chloride, exerted a catalytic influence on the elimination of hydrogen chloride, so that, on distillation in a vacuum, very little acid chloride was obtained, the chief product being a fourth, oily anhydride. This recalls the formation of bis-α-hydrin-done (2 : 2)-spiran by the action of phosphorus pentachloride on dibenzylmalonic acid (A., 1912, i, 179), in which case it is now found that the yield can be improved by the above process. Since the oil forms a hydrazone and is similar in deportment to methyl-, ethyl- and phenyl-α-hydrindones, it is 2-benzyl-1-hydrindone,

$$C_6H_4 \!\!<^{CH_2}_{CO}\!\!> CH \cdot CH_2Ph.$$
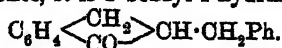
The solid anhydride, m. p. 145°, is bimolecular, does not yield a hydrazone, forms dibenzylacetic acid and 2-benzylhydrindone on hydrolysis with alcoholic potassium hydroxide, and dibenzylacetyl chloride and 2-chloro-2-benzyl-1-hydrindone under the influence of phosphorus pentachloride. It is therefore the *O*-dibenzylacetyl derivative of 1-hydroxy-2-benzylidene, the enolic form of 2-benzylhydrindone,

$$C_6H_4 \!\!<^{CH_2 \cdot C \cdot CH_2Pu}_{C \cdot O \cdot CO \cdot CH(CH_2Ph)_2} \!\!.$$
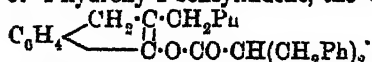
Dibenzylmalonic acid was boiled with thionyl chloride, and, after distilling off the dibenzylacetyl chloride at 203—204°/15 mm., the residue was extracted with light petroleum, leaving a 10% yield of *tetrabenzyl*cyclo*butan-1 : 3-dione*, $C_{32}H_{28}O_2$, which crystallised from benzene in colourless, light needles, m. p. 249—251°, and sublimed at 220—230°/18 mm. When hydrolysed by alcoholic sodium hydroxide, it gave s-*tetrabenzylacetone*, $CO[CH(CH_2Ph)_2]_2$, in the form of well-defined prisms, m. p. 124·5—125·5° (compare tetraphenylacetone,

Staudinger, A., 1911, i, 306). The ordinary *dibenzylacetic anhydride*, $C_{32}H_{30}O_3$, crystallised from alcohol in prisms, m. p. 75—76°, and formed dibenzylacetamide and ammonium dibenzylacetate when treated with ammonia in ether.

Dibenzylacetyl chloride, $C_{16}H_{15}OCl$, was prepared by the action of thionyl chloride on dibenzylacetic acid. The residue after distillation contained a little of the true anhydride, m p. 75—76°, but no *cyclo*butane derivative. The chloride is a viscous, almost colourless oil, b. p. 150°/0·25 mm., and the pale yellow, crystalline mass described by Schneidewind (A., 1888, 704), was probably not dibenzylacetyl chloride. After heating the oil for an hour at 245—255° in a low vacuum, and subsequently distilling off the unchanged chloride in a high vacuum, the residue was extracted with chloroform, precipitated by petroleum, and the 1-*dibenzylacetoxy-2-benzylindene*, $C_{32}H_{28}O_2$, was recrystallised from benzene in the form of shining, four or six-sided leaflets, m. p. 144—145°. On oxidation it yielded benzoic and phthalic acids and benzaldehyde, and on treatment with phosphorus pentachloride in chloroform suspension, it gave dibenzylacetyl chloride and

2-*chloro-2-benzylhydrindone*, $C_6H_4<^{CH_2\cdot CCl\cdot CH_2Ph}_{CO}$. The latter is insoluble in cold petroleum, forms long, colourless, glistening leaflets, m. p. 74—75°, and may be prepared by passing chlorine into a chloroform solution of 2-benzylhydrindone.

When dibenzylacetic acid is treated with a slight excess of phosphorus pentachloride, the chief product is the acid chloride, but when an insufficient amount of the reagent is employed and the product is evacuated at 200—250°, hydrogen chloride is eliminated and 2-*benzylhydrindone* distils over, mixed with a little unchanged acid. The distillate is added to an ethereal solution of ammonia, filtered, and re-distilled, giving a yellow, viscous, almost odourless oil, b. p. 223·5—224·5° (corr.)/20 mm. Phosphorus pentachloride converts it into 1-*chloro-2-benzylindene*, $C_6H_4<^{CH_2}_{CCl}>C\cdot CH_2Ph$, which crystallises in massive prisms, m. p. 64—65°, b. p. 206°(corr.)/13 mm., and yields benzaldehyde and benzoic and phthalic acids on oxidation. Its *dibromide*, $C_{16}H_{13}ClBr_2$, forms massive, sparkling, six-sided plates, m. p. 97—98°, which are hydrolysed in aqueous alcohol to 2-*bromo-2-benzylhydrindone*, $C_{16}H_{13}OBr$. The latter is best obtained by the action of bromine on β-benzylhydrindone, and forms colourless, sparkling, six-sided leaflets or prisms, m. p. 80—81°.

The *phenylhydrazone* of 2-benzylhydrindone, $C_{22}H_{20}N_2$, crystallises in light yellow, four-sided tablets, and, like the hydrazone of hydrindone itself (Kipping, T., 1894, **65**, 493), it has not a constant m. p. When the ketone is heated to 130° with an excess of phenylhydrazine, however, a *product*, $C_{28}H_{25}N_3$, is obtained in short, colourless prisms or tablets, m. p. 190—192°. J. C. W.

[Polymerisation.] CARL LIEBERMANN (*Ber.*, 1913, **46**, 2084—2086). —Polemical. A reply to Kronstein (this vol., i, 725).

D. F. T.

Some Derivatives of Diphenyleneacetic [Fluorene-9-carboxylic] Acid and Bisdiphenylenesuccinic [9 : 9'-Difluoryl-9 : 9'-dicarboxylic] Acid. ROBERT STOLLÉ and F. WOLF (*Ber.*, 1913, **46**, 2248—2252).—The action of thionyl chloride on fluorene-9-carboxylic acid leads to the formation of fluorene-9-carboxyl chloride, 9-chlorofluorene-9-carboxyl chloride, and 9 : 9'-difluoryl-9 : 9'-dicarboxyl chloride, according to the condition under which the action is carried out.

When heated for one to two hours with thionyl chloride in carbon tetrachloride solution, fluorene-9-carboxylic acid yields the corresponding chloride, which has m. p. 77° and reacts with ammonia and aniline yielding the amide, m. p. 251°, and anilide (compare Vorländer and Pritzsche, this vol., i, 724, and Staudinger, A., 1906, i, 861).
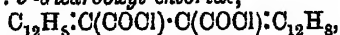
9 : 9'-*Difluoryl*-9 : 9'-*dicarboxyl chloride*,
$$C_{12}H_8{:}C(COCl){\cdot}C(COCl){:}C_{12}H_8,$$
obtained together with fluorene-9-carboxyl chloride by heating fluorene-9-carboxylic acid for several hours with thionyl chloride, forms colourless crystals, m. p. 213° (decomp.), and decomposes into bisdiphenylene-ethane (9 : 9'-difluoryl ; Graebe and Mantz, A., 1896, i, 442) when heated with concentrated hydrochloric acid. It is also produced by passing chlorine into a boiling solution of fluorene-9-carboxyl chloride in carbon tetrachloride. It reacts with sodium methoxide and sodium ethoxide, yielding the methyl ester, m. p. 237° (Kolvenbach, *Diss.*, Königsberg, 1897), and ethyl ester respectively (compare Staudinger, A., 1906, i, 825) ; the *anilide* forms a colourless powder, m. p. 250°.

If the action of thionyl chloride on fluorene-9-carboxylic acid or its chloride is continued for 200 hours, 9-chlorofluorene-9-carboxyl chloride (Klinger, A., 1912, i, 558) is produced.

Prolonged heating leads to the decomposition of thionyl chloride into chlorine and sulphur monochloride : $4SOCl_2 = 2SO_2 + 3Cl_2 + S_2Cl_2$. It is possible that the chlorinating action of thionyl chloride mentioned above is to be referred to this decomposition, but whether the formation of 9 : 9'-difluoryl-9 : 9'-dicarboxyl chloride is due to the direct oxidation of fluorene-9-carboxyl chloride, or to the interaction of the latter compound with 9-chlorofluorene-9-carboxyl chloride, has not yet been determined.   F. B.

New Method for the Ketonic Decomposition of β-Ketonic Esters. HANS MEERWEIN (*Annalen*, 1913, **398**, 242—250).—When heated at 200° with 0·5—1 volume of water, esters of β-ketonic acids undergo the ketonic decomposition quantitatively or nearly so. That the change is not due to an ordinary hydrolysis of the ester and subsequent elimination of carbon dioxide is proved by the fact that only those β-ketonic esters which are capable of enolising undergo the change. It is very probable that the enolic modification is the form which is concerned in the decomposition, since the facility with which the ketone is produced runs pari passu with the tendency of the β-ketonic ester to enolise ; thus, strongly acidic, cyclic β-ketonic esters such as ethyl succinosuccinate are decomposed most readily, then follow acyclic, non-alkylated esters such as ethyl acetoacetate and benzoyl-

acetate, and finally alkylated esters such as ethyl benzyl-, methyl-, or ethyl-acetoacetate, in the last case a temperatuie ot 250° being roquisite.

The author is of opinion that the course of the decomposition is represented by the scheme

$$R\cdot CO\cdot CH_2\cdot CO_2R' \rightarrow R\cdot CO\cdot CH\!:\!C(OH)\cdot OR' \xrightarrow{H_2O} R\cdot CO\cdot CH_3 + CO_2 + R'\cdot OH.$$
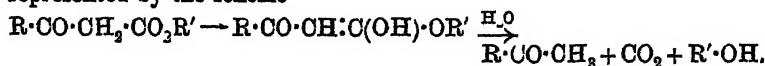
In support of this opinion are the facts that ethyl benzylmalonate is converted into ethyl β-phenylpropionate, and ethyl αγ-dicarb-ethoxyglutaconate into ethyl glutaconate, by water at 250° and 200° respectively.

The following changes are described : methyl 1-phenyl*cyclo*hexan-3-one-4 carboxylateacetate into methyl 1-phenyl*cyclo*hexan-3-one-5-acetate (A., 1908, i, 545), methyl *cyclo*pentanone-2-carboxylate into *cyclo*pentanone, ethyl succinosuccinate into *cyclo*hexan-1 : 4-dione, methyl benzoylacetate into acetophenone, ethyl acetoacetate into acetone, ethyl benzylacetoacetate into methyl β-phenylethyl ketone, ethyl methylacetoacetate into methyl ethyl ketone, and ethyl ethylacetoacetate into methyl propyl ketone. C. S.

Action of Hydroxylamine on Ketones of the Type R·CH:CH·CH:CH·CO·R. V.

RICCARDO CIUSA and G. B. BERNARDIS (*Atti R. Accad. Lincei,* 1913, [v], **22**, i, 708—711. Compare A., 1910, i, 684).—The substance $C_{26}H_{34}O_9N_4$, m. p. 213°, mentioned in the paper cited, contains one molecule of alcohol of crystallisation ; it does not react with bromine or with benzaldehyde, and it dissolves in alkalis. It is therefore composed of two molecules of the hydroxyl-amineoxime of cinnamylidenepyruvic acid united so as to saturate reciprocally their double linkings. The substance gives an insoluble, green copper salt, and a cherry-red coloration with iron salts ; in other respects it does not behave like an hydroxamic acid, and is to be regarded as an α-oximino-acid. The compound immediately yields a *sodium* salt, $C_{24}H_{26}O_8N_4Na_2$, when treated with sodium carbonate, and this salt yields with acids a *substance*, $C_{24}H_{28}O_8N_4$, m. p. 205° ; this compound has similar properties to the original one, but does not unite with alcohol. When the substance $C_{24}H_{28}O_8N_4$,EtOH, is boiled with dilute sulphuric acid, the *ethyl* ester, m. p. 207°, is obtained in small quantity.

When the action between hydroxylamine hydrochloride and ethyl cinnamylidenepyruvate is effected in the presence of sodium acetate, there is produced, in addition to the substance $C_{24}H_{28}O_8N_4$,EtOH, a sparingly soluble *sodium* salt, $C_{26}H_{31}O_8N_4Na$, which, on treatment with dilute sulphuric acid, furnishes an *isomeride* of the above-mentioned ethyl ester, m. p. 207°. This isomeride has m. p. 198°, and its properties resemble those of the compound of m. p. 207°.

From the mother liquors of the above reaction, the *oxime* of ethyl cinnamylidenepyruvate, $C_{14}H_{15}O_3N$, m. p. 181°, can be obtained. This substance is the sole product of the reaction when no sodium acetate is added.

When the sodium salt of the oxime of cinnamylidenepyruvic acid

(*loc. cit.*) is treated with dilute sulphuric acid, the corresponding *cinnamylidene-α-oximinopropionic acid* is produced; it crystallises with $\frac{1}{2}H_2O$, gives a green copper salt, and a cherry-red coloration with ferric salts. The above-mentioned sodium salt also yields the ethyl ester, m. p. 181°, already described.   R. V. S.

o-Thiolcinnamic Acid. Ch. CHMELEWSKI and PAUL FRIEDLÄNDER (*Ber.*, 1913, **46**, 1903—1908).—The above substance was prepared in order to examine its tendency to the formation of an anhydride analogous to coumarin; earlier experimental results appear to indicate that unsaturated ring systems of five carbon atoms and one sulphur atom are less easily produced, and are less stable than those corresponding with thiophen, but thiolcinnamic acid closely resembles coumaric acid in its behaviour towards dehydration.

o-Thiolcinnamic acid, $SH \cdot C_6H_4 \cdot CH:CH \cdot CO_2H$, was obtained from *o*-aminocinnamic acid by converting it into the corresponding *thiocyano*-compound, $CNS \cdot C_6H_4 \cdot CH:CH \cdot CO_2H$, needles, m. p. 175°, and then evaporating to dryness its solution in sodium hydroxide, together with sodium sulphide solution. The substance can be obtained more conveniently by introducing the solution of the diazocinnamic acid into a warm concentrated solution of sodium disulphide, and reducing the resultant *dithiocinnamic acid*, $(CO_2H \cdot CH:CH \cdot C_6H_4)_2S_2$, yellow needles, m. p. 221°, to the thiol acid by the action of zinc dust and sodium hydroxide solution. It was also prepared, through the diazo-compound, from the *xanthate*, $CO_2H \cdot CH:CH \cdot C_6H_4 \cdot S \cdot CS \cdot OEt$. *o*-Thiol-cinnamic acid, colourless needles, undergoes partial dehydration and oxidation on heating, consequently its m. p., 165°, is not sharp; its *methyl* ester forms tablets, m. p. 114°. o-*Methylthiolcinnamic acid*, $SMe \cdot C_6H_4 \cdot CH:CH \cdot CO_2H$, leaflets, m. p. 176°, obtained by the action of methyl sulphate on an alkaline solution, is more stable than the thiol acid. When heated above its m. p., or, much better, by boiling with acetic anhydride and subsequently distilling in a vacuum, *o*-thiol-cinnamic acid is dehydrated to *thiocoumarin* [1 : 2-*benzthiopyrone*],

$$C_6H_4 {\scriptstyle\diagup}^{\displaystyle CH:CH}_{\displaystyle S \!=\! CO},$$
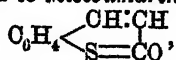
colourless needles, m. p. 80—80·5°, which is volatile with steam, and has an odour surprisingly like that of coumarin itself. It is insoluble in cold solutions of alkali, but dissolves in warm sodium hydroxide, and can be precipitated unaltered by mineral acids. As the acid undergoes isomeric change more readily than the corresponding coumaric acid, the warming with alkali must not be prolonged, otherwise *thiocoumarinic acid* is produced, of which the derived *methylthiol-coumarinic acid* has m. p. about 136°.

In behaviour towards oxidation, *o*-thiolcinnamic acid differs markedly from *o*-coumaric acid. Although frequently oxidation yields the corresponding dithio-acid, oxidation by ferric salts in neutral solution or, better, by potassium ferricyanide in alkaline solution causes elimination of hydrogen and of carbon dioxide with separation of thionaphthen, $C_6H_4 {\scriptstyle\diagup}^{\displaystyle CH}_{\displaystyle S}{\scriptstyle\diagdown} CH$.

Reduction of *o*-thiolcinnamic acid in alkaline solution by sod·um amalgam produces *o-thiolphenylpropionic acid*,

$$SH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CO_2H,$$
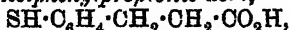
colourless needles, m. p. 118°, which above their m. p., or when heated with diluted sulphuric acid, undergo dehydration to *thiohydro-coumarin* [*dihydro*-1 : 2-*benzthiopyrone*], $C_6H_4 \underset{S}{\overset{CH_2 \cdot CH_2}{<}}_{CO}$, an oil of pleasant odour.   D. F. T.

Preparation of Tyrosine. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, **15**, 85—86).—The usual method of preparing tyrosine from silk is laborious and expensive. The method recommended is to obtain it from a pancreatic digest of caseinogen. The fluid on cooling deposits an abundant crystalline yield of tyrosine.   W. D. H.

Action of Nitric Acid on Heptachloro-*o*-quinocatechol Hemiether. C. LORING JACKSON and GEORGE L. KELLEY (*Amer. Chem. J.*, 1913, **49**, 435—473).—When heptachloro-*o*-quinocatechol hemiether, $OH \cdot C_6H_4 \cdot O \cdot C_6Cl_3O_2$ (Jackson and Carleton, A., 1908, i, 428), is warmed with glacial acetic acid and a little fuming nitric acid, the product sometimes yields a compound, m. p. 159—165° (decomp.), and sometimes a compound, m. p. 176—198° (decomp.); in each case the m. p. depends on the rate of heating.

The former compound, m. p. 159—165°, is probably the *tetrachloro-catechol hemiether* of *dichloronitrohydroxycyclopentadienecarboxylic acid*, $OH \cdot C_6Cl_4 \cdot O \cdot C_5Cl_2(OH)(NO_2) \cdot CO_2H$; it forms white or cream-coloured crystals.

The compound, m. p. 176—198°, is regarded as the *tetrachloro-catechol hemiether* of 2 : 4 : 5-*trichloro*-2-*nitro*-1 : 3-*dihydroxycyclopentene*-1-*carboxylic acid*, $OH \cdot C_6Cl_4 \cdot O \cdot C(OH) \underset{CCl}{\overset{CCl(NO_2) \cdot C(OH) \cdot CO_2H}{<}}_{CCl}$; it crystallises in nearly white needles, and is decomposed by boiling water with formation of tetrachlorocatechol, carbon dioxide, an oxide of nitrogen, and a tarry residue. The *methyl* ester, m. p. 221° (decomp.), forms clusters of creamy-white needles. On treating the compound (m. p. 176—198°) with methyl alcohol and sulphuric acid, it is converted into the *tetrachlorocatechol hemiether* of *methyl* 2 : 4 : 5-*trichloro*-2-*nitrocyclopentene*-1 : 3-*oxide*-1-*carboxylate*,

$$OH \cdot C_6Cl_4 \cdot O \cdot C \overset{CCl(NO_2)}{\underset{CCl=CCl}{<}}\!\!-O-\!\!>C \cdot CO_2Me,$$
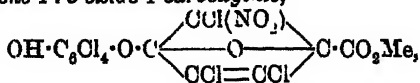
m. p. 221—228° (decomp.), which crystallises in rhombic plates or needles; its *acetyl* derivative, m. p. 189° (decomp.), forms white, rhombic prisms.

When the compound (m. p. 176—198°) is heated with acetic anhydride or acetyl chloride, it yields the *acetyl* derivative of the *tetra-chlorocatechol hemiether* of 2 : 4 : 5-*trichlorocyclopentadien*-1-*one*,

$$OAc \cdot C_6Cl_4O \cdot C \overset{CCl \cdot CO}{\underset{CCl:CCl}{<}},$$
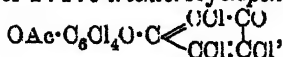
m. p. 165—168°, which crystallises in white, lustrous, rhombic plates;

on evaporating the mother liquor from this reaction, a viscous residue is obtained which when dissolved in benzene and treated with pyridine furnishes the *tetrachlorocatechol ether* of 2 : 5-*dichloro* 1 : 1-*diacetoxy-cyclopentadiene*, $C_6Cl_4O_2 \cdot C_5Cl_2(OAc)_2$, m. p. 188°, which forms white prisms or needles. The *tetrachlorocatechol hemiether* of 2 : 4 : 5-*tri-chlorocyclopentadien-1-one*, $OH \cdot C_6Cl_4O \cdot C {\displaystyle <^{CCl \cdot CO}_{CCl \colon CCl'}}$ m. p. 182—188° (decomp.), obtained by hydrolysing the acetyl derivative, crystallises in clusters of white needles. When a benzene solution of this compound or its acetyl derivative is treated with pyridine, the *tetrachlorocatechol ether* of *dichlorocyclopentadienone*,

$$C_6Cl_4 {\displaystyle <^{O \cdot C \colon CCl}_{O \cdot C \colon CCl}} > CO,$$
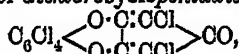
m. p. 264—272° (decomp.), is obtained, which forms thin, bright red, hexagonal plates and is converted by sodium methoxide into the *tetrachlorocatechol hemiether* of *dichloro-1-hydroxy-*1 : 4-*dimethoxycyclo-pentadiene*, $OH \cdot C_6Cl_4 \cdot O \cdot C_5Cl_2(OMe)_2 \cdot OH$, m. p. 175—180° (decomp.), which crystallises in white cubes ; the corresponding *diethoxy*-compound has m. p. 93°.

By the action of benzoyl chloride on the compound, melting at 176—198°, the *benzoyl* derivative of the tetrachlorocatechol hemi-ether of 2 : 4 : 5-trichloro*cyclo*pentadien-1-one,

$$OBz \cdot C_6Cl_4O \cdot C {\displaystyle <^{CCl \cdot CO}_{CCl \colon CCl'}}$$
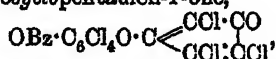
m. p. 172°, is obtained, which forms white, lustrous scales.

When a solution of hexachloromethoxy-*o*-quinocatechol hemiether, $OH \cdot C_6Cl_4 \cdot O \cdot C_6Cl_2O_2 \cdot OMe$ (Jackson and Kelley, A., 1912, i, 275), in glacial acetic acid is warmed with fuming nitric acid, it is converted into a substance, m. p. 202—208° (decomp.), which is probably the *tetrachlorocatechol hemiether* of *dichloronitrodihydroxymethoxycyclo-pentenecarboxylic acid*, $OH \cdot C_6Cl_4 \cdot O \cdot C_5Cl_2(NO_2)(OH)_2(OMe) \cdot CO_2H$; it forms white crystals, and yields an *acetyl* derivative, m. p. 146° (decomp.).

By the action of glacial acetic acid and fuming nitric acid on hexachloroethoxy-*o*-quinocatechol hemiether (Jackson and Kelley, *loc. cit.*), a compound, m. p. 210—215° (decomp.), is produced, which crystallises in rhombic plates or prisms, and is provisionally regarded as the *nitric acid* compound of the *tetrachlorocatechol hemiether* of *dichloro-ethoxy-o-quinone*, $OH \cdot C_6Cl_4 \cdot O \cdot C_6Cl_2O_2 \cdot OEt, HNO_3$. Another substance, m. p. 130—158° (decomp.), was also obtained in this reaction, which seems to be the corresponding compound containing $2HNO_3$.

E. G.

Quinonecarboxylic Esters. KARL BRUNNER (*Monatsh.*, 1913, 34, 913—930).—Although esters of substituted *p*-benzoquinone-carboxylic acids are known, previous attempts (von Rakowski and Leppert, A., 1875, 1197 ; Brunner, *Monatsh.*, 1881, 2, 464 ; Nef, A., 1887, 255 ; Juch, A., 1905, i, 701) to prepare *p*-benzoquinone-carboxylic acid have been unsuccessful. Since this failure was possibly attributable to the employment of aqueous solutions, the

author has been led to study the oxidation of methyl gentisate in the absence of water and has thus prepared *methyl* p-*benzoquinonecarboxylate* and a number of its derivatives.

When a solution of methyl gentisate in benzene is shaken with a mixture of silver oxide and potassium carbonate for five minutes at 40—50°, methyl p-benzoquinonecarboxylate, yellowish-red crystals, m. p. 53·5—54°, is obtained. The dry substance may be preserved unchanged for months in the dark. It is rapidly decomposed when warmed with water. When mixed in warm ethereal solution with an equimolecular quantity of methyl gentisate, it is converted into *methyl quinhydronecarboxylate*, dark red crystals with metallic glance, m. p. 85—86° which, when warmed with sulphurous acid and water, is transformed into methyl gentisate, m. p. 87°. When mixed with aniline in ethereal solution, methyl p-benzoquinonecarboxylate yields *methyl dianilino-p-benzoquinonecarboxylate*, $C_8H_4O_4(NHPh)_2$, deep red, silky needles, m. p. 202—203°.

Methyl cyanoquinolcarboxylate, $C_9H_7O_4N$, is formed when an aqueous solution of sodium cyanide is added to a cold acidified alcoholic solution of methyl p-benzoquinonecarboxylate. It has m. p. 225—226°, and dissolves sparingly in ether and benzene to yield solutions which have an intense blue fluorescence. Small quantities of a substance, m. p. above 220°, are obtained as a by-product. When treated with potassium hydroxide and acetic anhydride, methyl cyanoquinolcarboxylate yields a *diacetyl* derivative, colourless crystals, m. p. 107·5—108°.

Methyl cyanoquinolcarboxylate is converted by concentrated sulphuric acid at 100° into p-dihydroxyphthalimide, sulphur-yellow needles, m. p. 273—274°. This substance appears to be in all respects identical with that prepared by Thiele and Meisenheimer (A., 1900, i, 299), from dicyanoquinol, except that it gives up its water of crystallisation with greater readiness. This phenomenon apparently depends to some extent, however, on the size of the crystals. The *lead* salt, $C_8H_3O_4NPb,H_2O$, carmine needles, is also described.

When methyl cyanoquinolcarboxylate is successively treated with concentrated aqueous potassium hydroxide and sulphuric acid, p-dihydroxyphthalic acid is obtained in practically white crystals, m. p. 219—220° (decomp.). The air-dried acid appears to be anhydrous. According to Thiele and Günther (A., 1906, i, 744) it has m. p. 213° and contains $\frac{1}{2}H_2O$. The *lead* salt, $C_8H_4O_6Pb,\frac{1}{2}H_2O$, crystallises in leaflets. When sublimed in a vacuum at 230—240°, the acid is converted into p-dihydroxyphthalic anhydride, yellow, hygroscopic needles, m. p. 232—233° (compare Thiele and Günther, *loc. cit*), which yields the corresponding diacetyl derivative, m. p. 156—156·5°. The identity of these products obtained from methyl cyanoquinolcarboxylate with those obtained from dicyanoquinol by Thiele and Günther, leads the author to propose the annexed formula for the product examined by him.
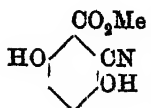
Ethyl p-*benzoquinonecarboxylate* is prepared by a method similar to that adopted for the methyl ester. Its isolation is more difficult, however, since it melts slightly above the ordinary

temperature and readily decomposes when in the liquid state. It forms yellowish-red leaflets, m. p. 22°, which decompose when preserved even at a low temperature. With aniline in ethereal solution, it yields *ethyl dianilino-p-benzoquinonecarboxylate*, dark red, almost black needles, m. p. 178—179°.   H. W.

Action of Bromine on Aliphatic-Aromatic Compounds.
HUGO BAUER and GUSTAV ENDRES (*J. pr. Chem.*, 1913, [ii], **87**, 545—552).—An account of the action of bromine on o- and p-benzylbenzoic acids, phenylphthalide, homophthalic acid, phthalidecarboxylic acid and di-p-nitrodiphenylmethane.

p-Benzylbenzoic acid reacts with bromine in the cold yielding a *tribromo*-derivative, which crystallises in slender scales, m. p. 218—220°. When heated with bromine for three or four hours in a sealed tube at 110—120°, it gives rise to *dibromotetraphenylethylenedi-p-carboxylic acid*, $CO_2H \cdot C_6H_8Br \cdot CPh \cdot CPh \cdot C_6H_8Br \cdot CO_2H$, m. p. 260—262°.

a-Phenylphthalide and bromine at 120° yields the dilactone of dihydroxytetraphenylethanecarboxylic acid (Ullmann, A., 1896, i, 563), which is also obtained from o-benzylbenzoic acid at 110—120°. If the action of bromine on o-benzylbenzoic acid is carried out at the ordinary temperature, the lactone is accompanied by a *bromo-o-benzylbenzoic acid*, m. p. 137°.

Phthalidecarboxylic acid, $CO{<}^{C_6H_4}_{O}{>}CH \cdot CO_2H$, and bromine at 120° yield hydrogen bromide, carbon dioxide, and phthalic anhydride; the same products are also obtained from homophthalic acid, $CO_2H \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$.

From the product of the action of bromine on di-p-nitrodiphenylmethane, only di-p-nitrobenzophenone could be isolated.   F. B.

Hydrogenation of Santonic Acid. A Dihydrosantonin. II.
GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 711—714. Compare this vol., i, 730).—The author discusses the question of the constitution of santonin in the light of the results obtained by himself and other recent workers, and points out that the production of a dihydrosantonin cannot be reconciled with the views of Wienhaus and von Oettingen (this vol., i, 474).

Dihydrosantonin, $C_{15}H_{20}O_8$, crystallises in long prisms, m. p. 99° (*loc. cit.*), and has $[a]_D^{18} +75.19°$ in 1·463% alcoholic solution. Its oxime, $C_{15}H_{21}O_8N$, forms tufts of colourless prisms, m. p. about 235°. The semicarbazone crystallises in colourless prisms, m. p. 243°.

R. V. S.

Constitution of Santonin.
ANGELO ANGELI (*Ber.*, 1913, **46**, 2233—2235).—The author points out that Asahina (this vol., i, 731), has overlooked the work of Angeli and Marino (A., 1907, i, 321) on the oxidation of santonin to heptanetetracarboxylic acid, the formation of which led them to the conclusion that santonin contains a bridged ring.   F. B.

The Ethers and Esters of Fluorescein. HANS VON LIEBIG (*J. pr. Chem.*, 1913, [ii], 88, 26—48) —In previous papers (A., 1912, i, 376; this vol., i, 79) the author has described four monomethyl ethers and esters of fluorescein, a strongly yellow form of m. p. 266°, two pale yellow ethers of m. p. 265° (corresponding with Fischer and Hepp's [A., 1895, i, 291] ether of m. p. 262°) and 272°, and also a colourless ether of m. p. 256—257°, obtained by hydrolysing the dimethyl ether of m p. 208° with ethyl alcoholic potassium hydroxide. It is now found that, during the hydrolysis, part of the methyl is replaced by ethyl, so that the colourless ether of m. p. 256—257° really consists of the lactone form of the monoethyl ether,

$$O{<}{}^{C_6H_3(OEt)}_{C_6H_3(OH)}{>}C{<}{}^{O-}_{C_6H_4}{>}CO,$$
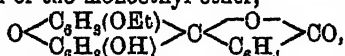
which, in a pure condition, crystallises in white prisms, m. p. 253—254°.

If the hydrolysis is carried out with methyl alcoholic potassium hydroxide, the colourless monomethyl ether of m. p. 272° is obtained. This ether represents the lactone form of the monomethyl ether, whilst the yellow ether of m. p. 266° has the quinonoid constitution

$$O{<}{}^{C_6H_3(OMe)}_{C_6H_3O}{>}C{\cdot}C_6H_4{\cdot}CO_2H;$$
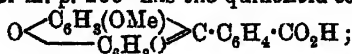
the ether of m. p. 265° (or 262°) is either a mixture or, more probably, a polymeric form similar to the quadrimolecular monomethyl ether described previously.

The monomethyl ester, obtained by warming fluorescein with methyl alcohol and sulphuric acid, has m. p. 282—283°, and not 252° as given by Feuerstein and Wallach (A., 1901, i, 723); the corresponding monoethyl ester has m p. 251—252°, and not 242°.

By methylating the monomethyl ester of fluorescein with methyl sulphate, Kehrmann and Dengler (A., 1909, i, 249) obtained a red compound of m. p. 176—177°, which they considered to be the methyl ester of the monomethyl ether of fluorescein The author finds, however, that the product of the action consists of a mixture of the dimethyl ether of m. p. 198° (Kehrmann's 3 : 6-dimethoxyfluorane) and Fischer and Hepp's (*loc. cit.*) coloured dimethyl ether of m. p. 208°.

When the dimethyl ether of m. p. 198° is heated with methyl alcohol and concentrated hydrochloric acid, and the resulting solution diluted with water and saturated with sodium chloride, a *hydrochloride* of the trimethyl ether of fluorescein is obtained which, after precipitation from alcoholic solution by means of ether, has the composition $4C_{23}H_{20}O_6,5HCl,10H_2O$ (compare Kehrmann and Scheunert, A., 1912, i, 1034); the addition of concentrated hydrochloric acid to a warm aqueous solution of this chloride causes the precipitation of a *chloride* of the composition $2C_{22}H_{18}O_5,3HCl,8H_2O$, crystallising in stout, orange prisms having a bluish glance. The *sulphate* of the trimethyl ether of fluorescein is prepared by heating the dimethyl ether of m. p. 198° with methyl alcohol and sulphuric acid; it has m. p. 226°.

That the above salts are derivatives of the trimethyl ether to fluorescein has been established by reducing the sulphate with zinc dust and glacial acetic acid, when the trimethyl ether of fluorescin

was obtained, identical with that previously prepared by the direct methylation of fluorescein with methyl sulphate.

Oxidation of the trimethyl ether of fluorescin by means of lead dioxide in hot glacial acetic acid solution gives rise to the dimethyl ether of fluorescein, having m. p. 198°, and the above-mentioned trimethyl ether of fluorescein, which was isolated in the form of its *nitrate*, $C_{22}H_{16}O_5,HNO_3$, crystallising in light yellow leaflets.

Hydrolysis of the trimethyl ether of fluorescin with alcoholic potassium hydroxide leads to the formation of the *dimethyl ether* of fluorescin, $C_{22}H_{18}O_5$, which crystallises from alcohol in white needles, m. p. 204—205°, and is also obtained, together with the trimethyl ether, by methylating fluorescin with aqueous potassium hydroxide and methyl sulphate.

When oxidised by means of lead dioxide in hot glacial acetic acid solution the dimethyl ether of fluorescin yields the dimethyl ether of fluorescein of m. p. 198°.

The monomethyl ether of fluorescein of m. p. 265° forms a potassium salt, $C_{21}H_{13}O_5K,C_{21}H_{12}O_5K_2,4H_2O$.

When heated with ethyl iodide and alcoholic potassium hydroxide, fluorescein yields a quadrimolecular *monoethyl ether* of the composition $3C_{20}H_{12}O_5,C_{22}H_{16}O_5,H_2O$, m. p. 330—331°, in addition to the diethyl ethers of m. p. 159° and 181°.

When esterified with methyl alcohol and sulphuric acid the mono-methyl ethers of fluorescein of m. p. 265°, 266°, and 272° are converted into the dimethyl ether-ester of m. p. 208°, $OMe·C_{19}H_{10}O_2·CO_2Me$, which crystallises in orange-yellow needles or dark red prisms, and is precipitated in the form of its *sulphate*, $2C_{22}H_{16}O_5,H_2SO_4,H_2O$, dark red, prismatic crystals (decomp. 140°) by the addition of water to the product of the esterification.

If, after esterification, the mixture is treated with aqueous sodium hydroxide and the precipitated ester purified by conversion into the *hydrochloride*, $C_{22}H_{16}O_5,HCl,2H_2O$, a second modification of the dimethyl ether-ester is obtained; this crystallises in yellowish-red prisms, m. p. 198°, and on repeated crystallisation from ethyl acetate is transformed into the dimethyl ether of m. p. 208°.

The *ethyl* ester of the monomethyl ether of fluorescein,

$$OMe·C_{19}H_{10}O_2·CO_2Et,$$

prepared by esterifying the monomethyl ether with ethyl alcohol and sulphuric acid, has m. p. 194—195°, and yields a *hydrochloride*,

$$C_{23}H_{18}O_5,HCl,$$

crystallising in yellowish-red needles; the *methyl* ester of the mono-ethyl ether of fluorescein, $OEt·C_{19}H_{10}O_2·CO_2Me$, obtained in a similar manner, crystallises in yellowish-red prisms or needles, m. p. 216°; the *ethyl* ester of the monoethyl ether forms a *hydrochloride*,

$$OEt·C_{19}H_{10}O_2·CO_2Et,HCl,$$

crystallising in yellowish-red needles.

A solution of the sulphate of the monomethyl ester of fluorescein (m. p. 282—283°) in sodium hydrogen carbonate deposits a *sodium* salt of the composition $C_{21}H_{14}O_5,NaHSO_4$ as a fine red powder.

According to the author (A., 1912, i, 381), the salts of fluorescein and its ethers with acids owe their solubility in water to the rupture

of the oxygen bridge of the pyrone ring and formation of compounds having the structure represented in (I).

(I.)

(II.)

(III.)
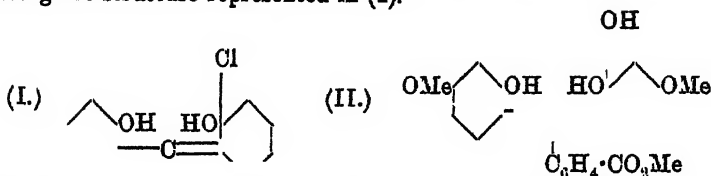
If this view is correct the salts of the trimethyl ether of fluorescein should give rise on hydrolysis to the compound (II), which with potassium hydroxide would form a quinonoid having the annexed formula (III), and, from analogy with the quinonoid salts of quinolphthalein and 4:5-dinitrofluorescein (this vol., i, 80; compare also Baeyer, A., 1910, i, 249), this salt should have a blue colour.
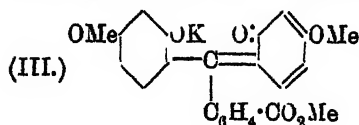
Such an o-quinonoid *potassium* salt has been prepared by triturating the trimethyl ether of fluorescein with 33% aqueous potassium hydroxide. It has the composition $C_{22}H_{19}O_6K,H_2O$, and rapidly decomposes when kept, yielding a brown *substance*, which has m. p. about 120°, with previous sintering, and dissolves in methyl and ethyl alcohols, yielding solutions coloured respectively pure green and brownish olive-geeen; from these solutions the addition of alkalis causes the separation of the dimethyl ether of fluorescein.

When freshly prepared and treated with water, the blue potassium salt partly dissolves with the formation of a deep blue solution, from which acetic acid precipitates a *hydrate* of the trimethyl ether-ester of fluorescein, $C_{22}H_{20}O_6,H_2O$, in yellow flocks. This melts and loses water at 173°. It dissolves in alkali hydroxides with a blue colour, and is, therefore, considered to be the parent substance of the blue potassium salt. On treatment with water, the greater part of the blue potassium salt is converted into an insoluble brown *substance*, which crystallises in needles, is insoluble in alkalis, and probably represents the trimethyl ether-ester of fluorescein of the following constitution : $O<^{C_6H_3(OMe)}_{C_6H_3(OMe)}>C(OH)·C_6H_4·CO_2Me$.   F. B.

[Fluorescein.] HANS VON LIEBIG (*J. pr. Chem.*, 1913, [ii], **88**, 96).—A correction. Owing to an error in the thermometer the m. p.'s of a number of ethers and esters of fluorescein recorded in previous papers (A., 1912, i, 376; this vol., i, 79) are too high.

The lactone form of the monomethyl ether has m. p. 266° (not 272°), the quinonoid form 259° (not 266°), and the monomethyl ester m. p. 274—275° (not 282°). The lactone form of the monomethyl ether, previously described as melting at 253—254°, has m. p. 247—248°. The monoethyl ester has m. p. 247°.   F. B.

Fluorescein Methyl Ethers. OTTO FISCHER and EDUARD HEPP (*Ber.*, 1913, **46**, 1951—1959. Compare A., 1895, i, 291).—A reply to

von Liebig (this vol., i, 79) and to Kehrmann and Dengler (A., 1909, i, 249). The divergence of the results of these workers from those previously obtained by the authors is probably to be attributed to impure fluorescein. The fluorescein used by the authors was always previously purified through the diacetyl derivative.

Methylation of purified fluorescein by methyl iodide and alcoholic potassium hydroxide gives as main product the orange-red dimethyl ether, m. p. 208°, together with a little of the colourless lactonic dimethyl derivative, m. p 197—198°, which previously escaped detection. A similar result is obtained by the application of diazomethane in nitrobenzene solution. Fluorescein monomethyl ester, m p. 282°, obtained by the interaction of fluorescein and methyl alcohol in the presence of sulphuric acid or hydrogen chloride, also gives a similar product to the above whether further methylated in methyl alcohol by methyl iodide and potassium hydroxide or in nitrobenzene solution by methyl sulphate. In the latter case no indication whatever of a substance, m. p. 176—177° (Kehrmann and Dengler, *loc. cit*), was observed.

By hydrolysis of fluorescein dimethyl ether, m. p. 208°, with methyl-alcoholic potassium hydroxide, the colourless lactonic fluorescein monomethyl ether, m. p. 265—266°, can be obtained; on methylation of this by methyl sulphate in nitrobenzene solution the chief product is the dimethyl ether, m. p. 197—198°.   D. F. T.

Substituted Crotonolactoneacetic [αγ-Monolactones of γ-Hydroxydihydromuconic] Acids. ERICH BESCHKE [with GEORG KOHRES and F. MARSCHALL] (*Annalen*, 1913, 398, 265—298).—The interaction of phenanthraquinone, ethyl bromoacetate, and zinc in boiling benzene leads to the formation of *γ-hydroxy-βγ-diphenylene-Δ²-dihydromuconic acid αγ-lactone*,
$$\begin{array}{c} C_6H_4\cdot C(CH_2\cdot CO_2H)\cdot O \\ C_6H_4\cdot C\!\!=\!\!=\!\!=\!\!=\!\!CH \end{array}\!\!\!>\!CO, \text{ m. p.}$$
216°, colourless crystals, which exhibits considerable stability towards dilute alkaline potassium permanganate, zinc dust and acetic acid, and bromine. Its *sodium* salt, $C_{18}H_{11}O_4Na$, reacts with aqueous bromine to form, after acidification, *α-bromo-γ-hydroxy-βγ-diphenylene-Δ²-dihydromuconic acid αγ-lactone*, $C_{18}H_{11}O_4Br$, m. p 195°, by the reduction of which by zinc dust and alcohol the original acid is regenerated.

The addition of saturated aqueous sodium hydroxide to a boiling alcohol solution of γ-hydroxy-βγ-diphenylene-Δ²-dihydromuconic acid γ-lactone yields *sodium γ-hydroxy-βγ-diphenylene-Δ²-dihydromuconate*,
$$\begin{array}{c} C_6H_4\cdot C(OH)\cdot CH_2\cdot CO_2Na \\ C_6H_4\cdot C\!\!:\!\!CH\cdot CO_2Na \end{array}$$, an aqueous solution of which is reduced by
3% sodium amalgam to *phenanthrene-9 : 10-diacetic acid*,
$$\begin{array}{c} C_6H_4\cdot C\cdot CH_2\cdot CO_2H \\ C_6H_4\cdot C\cdot CH_2\cdot CO_2H' \end{array}$$
m. p. 305°, colourless crystals. This acid forms an *ethyl* ester, $C_{22}H_{22}O_4$, m. p 94°, and is converted by heating into *2-ketophenanth-hydrindene*,
$$\begin{array}{c} C_6H_4\cdot C\cdot CH_2 \\ C_6H_4\cdot C\cdot CH_2 \end{array}\!\!\!>\!CO, \text{ m. p. 219°,}$$ colourless leaflets (*oxime*, m.p. 258° [decomp.])
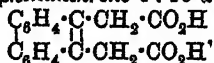
γ-Hydroxy-βγ-diphenylene-Δ^α-dihydromuconic acid αγ-lactone forms an *ethyl* ester, $C_{20}H_{16}O_4$, m. p. 104°, from which the acid is regenerated by hydrolysis with acids. However, when a cold alcoholic suspension of the ester is treated with sodium ethoxide and the resulting yellow solution is acidified, *ethyl hydrogen βγ- diphenylenemuconate*,

$$\begin{array}{l} C_6H_4 \cdot C{:}CH \cdot CO_2Et \\ C_6H_4 \cdot C{:}CH \cdot CO_2H \end{array},$$ is obtained as a viscous, yellow mass which by

keeping or warming changes to the *ethyl* ester, m. p. 234°, colourless crystals, of the αδ-*lactone* of δ-hydroxy-βγ-diphenylene-Δ^α-dihydro-

muconic acid, $$\begin{array}{l} C_6H_4 \cdot CH \cdot CH(CO_2Et) \\ C_6H_4 \cdot C{:}CH \longrightarrow CO \end{array}>O,$$ m.p. 280° (decomp.), colourless

crystals. By treating a boiling alcoholic solution of ethyl γ-hydroxy-βγ-diphenylene-Δ^α-dihydromuconic acid αγ-lactone with concentrated aqueous sodium hydroxide, *sodium-βγ diphenylenemuconate*,

$$\begin{array}{l} C_6H_4 \cdot C{:}CH \cdot CO_2Na \\ C_6H_4 \cdot C{:}CH \cdot CO_2Na \end{array},$$
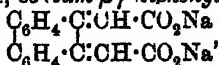
is obtained, from which a yellow acid is obtained by acidification; by recrystallisation the yellow acid, *βγ diphenylenemuconic acid*, is changed into the lactone, m. p. 280° (decomp.), of δ hydroxy-βγ-diphenylene-Δ^α-dihydromuconic acid. An aqueous alkaline solution of βγ-diphenylenemuconic acid is reduced by sodium amalgam to phenanthrene-9 . 10 diacetic acid, from which phenanthraquinone is obtained by oxidation with chromic and acetic acids.

By oxidation with chromic and acetic acids at 75° and finally at 90°, the lactone of δ hydroxy-βγ-diphenylene-Δ^α-dihydromuconic acid is

converted into the *lactone*, $$\begin{array}{l} C_6H_4 \cdot CH \cdot CH_2 \cdot O \\ C_6H_4 \cdot CH \cdot CO - CO \end{array},$$ m. p. 211°, colourless

crystals, which forms a *phenylhydrazone*, $C_{23}H_{18}O_2N_0$, m. p. 234°, faintly yellow leaflets, and o-*aminoanilino* derivative, $C_{23}H_{18}O_2N_2$, m. p. 236°, with o-phenylenediamine, and is oxidised by chromic acid in

boiling glacial acetic acid to the *lactone*, $$\begin{array}{l} C_6H_4 \cdot C \cdot CH_2 \cdot O \\ C_6H_4 \cdot C \cdot CO - CO \end{array},$$ m. p. 302°,

yellow crystals. The latter lactone, which is more conveniently obtained directly by the oxidation of the lactone of δ hydroxy-βγ-diphenylene-Δ^α-dihydromuconic acid, forms a *phenylhydrazone*, m. p. 292°, yellow needles, *anilino*-derivative, $C_{23}H_{15}O_2N$, m. p 263°, yellow needles, o-*aminoanilino*-derivative, m. p. 269° (decomp.), and *phenazine*, $C_{23}H_{14}ON_2$, m. p. 271°, yellowish-red needles.   C. S.

Synthesis of Derivatives of *dicyclo*-[1,3,3]-Nonane. I. Hans Meerwein and Wilhelm Schurmann (*Annalen*, 1913, **398**, 196—242). —Derivatives of *dicyclo*-[1 : 3 : 3]-nonane (annexed formula) have

$$\begin{array}{l} CH_2 \cdot CH - CH_2 \\ CH_2 \quad CH_2 \quad CH_2 \\ CH_2 \cdot CH - CH_2 \end{array}$$

been prepared from formaldehyde and ethyl malonate by a very simple and smooth reaction.

Perkin, in conjunction with Haworth (T., 1898, **73**, 330) and Bottomley (T., 1900, **74**, 294), has shown that formaldehyde and malonic esters condense to form, under different conditions, methylenemalonic esters, methylenebismalonic esters, or pentane-ααγγεε-hexacarboxylic esters. By this

method the authors have prepared *methyl methylenemalonate*,

$$CH_2 : C(CO_2Me)_2,$$

as a mixture, b. p. 150—180°/15 mm., of the uni- and bi-molecular forms (the latter is an amorphous, white powder which is depolymerised by distillation at 200—203°), and also *methyl pentane-aαγγεε-hexa-carboxylate*, $CH(CO_2Me)_2 \cdot CH_2 \cdot C(CO_2Me)_2 \cdot CH_2 \cdot CH(CO_2Me)_2$, m. p. 62—63°, hard, colourless prisms. The latter, which can also be obtained by the interaction of methyl methylenebismalonate and methyl methylenemalonate in alcoholic sodium methoxide at the ordinary temperature, is converted by boiling methyl alcoholic sodium methoxide into methyl carbonate and *methyl* cyclohexan-1-one-2 : 4 : 4 : 6-*tetra-carboxylate*, $CO \overset{CH(CO_2Me) \cdot CH_2}{\underset{CH(CO_2Me) \cdot CH_2}{<}} > C(CO_2Me)_2$, m. p. 121—122°, colour-less, rhombic prisms, methyl *bicyclo* [1,3,3] - nonane-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate (see below) being also formed. Methyl *cyclo*hexan-1-one - 2 : 4 : 4 : 6-tetracarboxylate exists as the ketonic modification in the solid state, but is rapidly enolised by alcohol, the solution in this solvent producing a reddish-violet coloration with ferric chloride. By acidifying a solution of the ester in alcoholic sodium methoxide, the enol is precipitated as a viscous oil, the ethereal solution of which deposits almost quantitatively the ketonic modification after a short time. This property of rapidly ketonising is utilised to separate the ester from the accompanying *dicyclo*nonanedionetetra-carboxylate.

By heating with half volume of water at 200° for thirty minutes (compare following extract), methyl *cyclo*hexan-1-one-2 : 4 : 4 : 6-tetra-carboxylate undergoes the ketonic decomposition and yields *methyl* cyclo*hexan-1-one-4 : 4-dicarboxylate*, b. p. 160—161°/14 mm., which has no acid properties, does not give a coloration with ferric chloride, forms a *semicarbazone*, m. p. 190° (decomp.), and *dicinnamylidene* derivative, $C_{28}H_{26}O_5$, m. p. 186°, yellow needles dissolving to a blue solution in concentrated sulphuric acid, and yields Perkin's *cyclo*hexan-1-one-4-carboxylic acid (T., 1904, **85**, 421; 1906, **89**, 1648) by hydrolysis.

All the substances, namely, methyl methylenemalonate and methyl methylenebismalonate, and methyl pentane-aαγγεε-hexacarboxylate, produced by the interaction of formaldehyde and methyl malonate,

$$\begin{array}{c}
CH_2 \cdot C(CO_2Me) \cdot CO \\
CO_2Me \cdot CH \quad CH_2 \\
CO - C(CO_2Me) \cdot CH_2
\end{array}$$

yield more or less *methyl* bicyclo-[1,3,3]-*nonan*-2 :6-*dione*-1 : 3 : 5 : 7-*tetracarboxylate* (annexed formula), m. p. 163—164°, colourless prisms, by boiling with concentrated methyl-alcoholic sodium methoxide, the best yield being obtained by using methyl methylenebismalonate (1 mol.) and methyl methylene-malonate (2 mols.).

The constitution of the *dicyclo*nonane derivative, which can also be prepared by heating methyl malonate (4 mols.) and methylene iodide (3 mols.), or methyl *cyclo*hexan-1-one-2 : 4 : 4 : 6-tetracarboxylate and methyl methylenemalonate, with methyl alcoholic sodium methoxide, is proved, not only by the preceding method of preparation, but also by the following reactions.

Methyl *dicyclo*-[1,3,3]-nonan-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate develops a reddish-violet coloration with alcoholic ferric chloride, forms a pale green *copper* derivative and a crystalline *disodium* derivative, $C_{17}H_{18}O_{10}Na_2$, and possesses pronounced acid properties, indicating that the substance is a cyclic

$$CH_2 \cdot C(CO_2Me) \cdot CO$$
$$CH_2 \quad CH_2 \qquad CH_2$$
$$CO-C(CO_2Me) \cdot CH_2$$
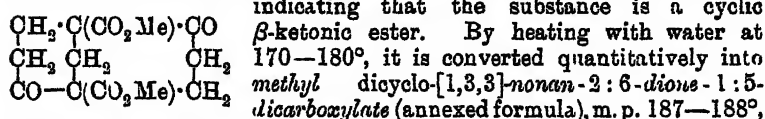
β-ketonic ester. By heating with water at 170—180°, it is converted quantitatively into *methyl* dicyclo-[1,3,3]-*nonan*-2 : 6-*dione*-1 : 5-*dicarboxylate* (annexed formula), m. p. 187—188°, colourless prisms or quadratic plates. This ester is insoluble in alkalis and does not develop a coloration with ferric chloride. However, it still contains two β-ketonic groups because it reacts
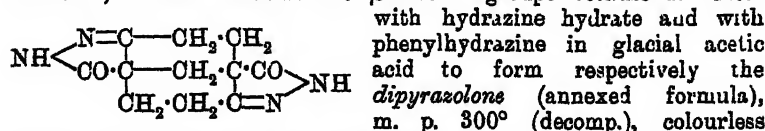
$$NH \begin{matrix} N=C-CH_2 \cdot CH_2 \\ CO \cdot C-CH_2 \cdot C \cdot CO \\ CH_2 \cdot CH_2 \cdot C=N \end{matrix} NH$$

with hydrazine hydrate and with phenylhydrazine in glacial acetic acid to form respectively the *dipyrazolone* (annexed formula), m. p. 300° (decomp.), colourless prisms, and corresponding *diphenyldipyrazolone*, m. p. 270°, pale yellow leaflets.

The decomposition of methyl *dicyclo*-[1,3,3]-nonan-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate by dilute alkali hydroxide is too profound to be of any service, but by hydrolysis by aqueous barium hydroxide at 105° and acidification of the resulting barium salt, the ester yields 3 : 7-*dimethyl* 1 : 5-*dihydrogen* dicyclo-[1,3,3]-*nonan*-2:6-*dione*-1 : 3 : 5 : 7-*tetracarboxylate*, m. p. 205—207° (decomp.), small prisms or needles, which gives a violet coloration with ferric chloride, regenerates the original ester, m. p. 163—164°, by treatment of its silver salt with methyl iodide, and is converted by heating into *methyl* dicyclo-[1,3,3]-*nonan*-2 : 6-*dione*-3 : 7-*dicarboxylate*, $C_{13}H_{16}O_6$, m. p. 136—137°, colourless prisms. The latter is soluble in alkalis, develops a reddish-violet coloration with ferric chloride, and forms a *dipyrazolone*, $C_{11}H_{12}O_2N_4$, decomp. above 300°, and *diphenyldipyrazolone*, $C_{23}H_{30}O_2N_4$, decomp. above 300°, thus indicating that the original *dicyclo*nonane derivative, methyl *dicyclo*-[1,3,3]-nonan-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate, must contain four β-keto-groups.
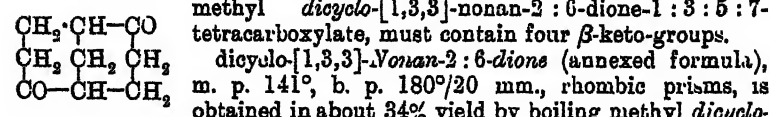
$$CH_2 \cdot CH-CO$$
$$CH_2 \quad CH_2 \quad CH_2$$
$$CO-CH-CH_2$$

dicyclo-[1,3,3]-*Nonan*-2 : 6-*dione* (annexed formula), m. p. 141°, b. p. 180°/20 mm., rhombic prisms, is obtained in about 34% yield by boiling methyl *dicyclo*-nonanedionetetracarboxylate or methyl *dicyclo*nonanedione-1 : 5-dicarboxylate with dilute hydrochloric acid, or quantitatively by heating 3 : 7-dimethyl 1 : 5-dihydrogen *dicyclo*nonanedionetetracarboxylate, or methyl *dicyclo*nonanedione-3 : 7-dicarboxylate with water at 200°. *dicyclo*Nonanedione is volatile with steam, forms a *diphenylhydrazone*, $C_{21}H_{24}N_4$, and a *di-oxime*, $C_9H_{14}O_2N_2$, m. p. 205—206° (decomp.), regular octahedra, and is stable to potassium permanganate, these reactions indicating that the substance is a dicyclic diketone. It condenses very readily with alcoholic benzaldehyde, or cinnamaldehyde in the presence of a little concentrated sodium hydroxide, yielding 3 : 7-*dibenzylidene*dicyclo-[1,3,3]-*nonan*-2 : 6-*dione*, $C_{23}H_{20}O_2$, m. p. 201°, faintly yellow needles, and the *dicinnamylidene* derivative, $C_{27}H_{24}O_2$, m. p. 246°, pale yellow powder, which dissolve in concentrated

sulphuric acid with a pale yellow and orange-red colour respectively. The significance of these slight colorations is important, because Wallach, Stobbe, and others have shown that the dibenzylidene and dicinnamylidene derivatives of cyclic ketones of the type

$$[CH_2]_x \!\!<\!\! \begin{array}{c} C(:CHAr)\!\!-\!\! \\ C(:CHAr)\!\!- \end{array} \!\!\!>\!\! CO$$
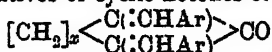
develop intensely yellow and violet colorations respectively with concentrated sulphuric acid. Hence the inference is drawn that only one methylene group is attached directly to a carboxyl group in the *dicyclo*-nonanedione.

The oxidation of *dicyclo*nonanedione by warm nitric acid, D 1·2, yields Guthzeit and Engelmann's pentane-$a\beta\delta\epsilon$ tetracarboxylic acid (*anhydride*, $C_9H_8O_8$, m. p. 161°; *methyl* ester, $C_{13}H_{20}O_8$, m. p. 60°, b. p. 210°/20 mm.). The formation of this acid proves that the diketone must have either the formula assigned to it by the authors (which is proved by the formation of methyl *dicyclo*nonanedionetetra-carboxylate, and therefore indirectly of the diketone, from a substance already containing a *cyclo*hexane ring [see above]) or the formula

$$CH_2 \!\!<\!\! \begin{array}{c} CO\!\!-\!\! \\ CH_2 \end{array} \!\!\!>\!\! CH \cdot CH_2 \cdot CH \!\!<\!\! \begin{array}{c} CO\!\!- \\ CH_2 \end{array} \!\!\!>\!\! CH_2 \;;$$ against the latter tells the

fact that the formation of a *cyclo*butane derivative has never been observed when there is a possibility for the reaction to produce a *cyclo*hexane derivative.   C. S.

Quantitative Investigation of the Photochemical Transformation of o-Nitrobenzaldehyde into o Nitrosobenzoic Acid. FRITZ WEIGERT and LUDWIG KUMMERER (*Ber.*, 1913, **46**, 1884—1885. Compare this vol., ii, 370; Kailan, *ibid.*, i, 51, 733).—A further criticism of Kailan's work on this subject.   F. B.

Quantitative Investigation of the Photochemical Transformation of o-Nitrobenzaldehyde into o-Nitrosobenzoic Acid. II. ANTON KAILAN (*Ber.*, 1913, **46**, 2175—2179. Compare this vol., i, 51).—In reply to Weigert and Kummerer's criticism (this vol., ii, 370) that the titration of o-nitrosobenzoic acid using phenolphthalein is not trustworthy in presence of much o-nitrobenzaldehyde, the author shows that the method gives satisfactory results.   J. C. W.

Bromination of Certain Ketones and of Some Secondary Hydroaromatic Alcohols. FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1913, **156**, 1840—1841. Compare A., 1912, i, 567).—Bromination was effected by the addition of a solution of the ketone or alcohol in carbon tetrachloride to an excess of bromine dissolved in the same solvent. After six hours, excess of bromine and carbon tetrachloride were removed by means of a current of air.

1-Methyl-2-*cyclo*hexanone yielded *tetrabromomethylcyclohexanone*, small, white needles, m. p. 105—107°, together with a small quantity of a mixture of tribromomethyl*cyclo*hexanones which could not be separated from one another. 1-Methyl-2-*cyclo*hexanol gave a poor yield of a mixture of tribromomethyl*cyclo*hexanones.

1-Methyl-3-*cyclo*hexanone was practically quantitatively converted

into a tribromomethyl*cyclo*hexanone. The latter was very difficult to purify, but had m. p. 55—58°.

1-Methyl-4-*cyclo*hexanone yielded a *tetrabromo*-derivative, white needles, m. p. 79°. The same substance was obtained from 1-methyl-4-*cyclo*hexanol.

1 : 3-Dimethyl-4-*cyclo*hexanone gave a *tetrabromo*-derivative, white prisms, m. p. 62—63°.

The bromo-derivatives of the homologues of *cyclo*hexanone a.e somewhat unstable. At temperatures slightly above their m p.'s, they are decomposed into bromine, hydrogen bromide, and bromo-phenols. The same transformation occurs slowly at the ordinary temperature under the influence of light. H. W.

Catalytic Hydrogenation of the Two Methyl*cyclo*pentanones. MARCEL GODCHOT and FELIX TABOURY (*Bull. Soc. chim.*, 1913, [iv], 13, 591—599).—It is shown that the reduction of the methyl*cyclo*pentanones by Sabatier and Senderens' method is quite analogous to that of *cyclo*pentanone (A., 1911, i, 385 ; 1912, i, 34), the products being the corresponding methyl*cyclo*pentanols and dimethyl*cyclo*pentyl*cyclo*pentanones, the latter predominating (compare Zelinsky, A., 1911, i, 988).

1-Methyl*cyclo*pentan-3-one yields 1-methyl*cyclo*pentan-3-ol (*phenylurethane*, m. p. 82°, colourless needles from alcohol) and 3-*methyl*cyclo*pentyl-2′(or 3′)-*methylcyclopentan-5′-one* (annexed formulæ), D_{16}^{16} 0·9365,

n_D^{16} 1·4700, b. p. 245°, a colourless liquid having an odour of menthol ; it yields a *semicarbazone*, m. p. 137°, crystallising in needles, and with hydroxylamine a *product*, m. p. 75—100°, which is probably a mixture of two stereoisomeric oximes.

$$\begin{array}{l}\text{CH}_2\text{---CH}_2\\ \text{CHMe·CH}_2\end{array}\!\!>\!\text{CH·CH}\!<\!\!\begin{array}{l}\text{CO---CH}_2\\ \text{CH}_2\text{·CHMe}\end{array}\ \text{or}$$

$$\begin{array}{l}\text{CH}_2\text{---CH}_2\\ \text{CHMe·CH}_2\end{array}\!\!>\!\text{CH·CH}\!<\!\!\begin{array}{l}\text{CO---CH}_2\\ \text{CHMe·CH}_2\end{array}$$

Attempts to prepare 1-methyl*cyclo*pentan-2-one by (1) the action of magnesium methyl iodide on 1-chloro*cyclo*pentan-2-one and (2) the action of methyl iodide on *cyclo*pentanone in presence of sodamide were unsuccessful; the second reaction yielded *cyclo*pentylidene-3-methyl*cyclo*pentan-2-one, of which the *oxime*, m. p. 85°, colourless needles, and the *semicarbazone*, m. p. 193°, were prepared.

The 1-methyl*cyclo*pentan-2-one required was prepared by Bouveault's method (A., 1900, i, 171). On reduction by nickel at 150°, 1-methyl-*cyclo*pentan-2-ol, D_{16}^{16} 0·9238, n_D 1·4466, b. p. 146—147° (*phenylurethane*, m. p. 84°), was obtained with 2-*methyl*cyclopentyl-3′-methyl-cyclo*pentan-2′-one* as a principal product. The latter has D_{16}^{16} 0·9238, n_D 1·4724, b. p. 239—241°, and is a colourless liquid with an odour of menthol ; it yields a *semicarbazone*, m. p. 202—203°, crystallising from alcohol in needles. Looft (A., 1894, i, 405) has already prepared a methyl*cyclo*pentanol, which may be identical with that described above. T. A. H.

Ketimines. CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1913, 156, 1801—1806).—The authors have succeeded in

isolating a series of ketimines of the general formula CR_2:NH, the bromomagnesium derivatives of which are formed as intermediate products in the preparation of ketones by the action of Grignard's reagents on nitriles.

For the preparation of purely aromatic ketimines, the solid product of the action of the aryl-nitrile on the magnesium aryl haloid is brought, little by little, into a mixture of crushed ice and ammonium chloride, the mixture extracted with ether, the ethereal solution dried and saturated with dry hydrogen chloride. The precipitated imine-hydrochloride is filtered, suspended in ether, and decomposed by dry ammonia gas. After removal of ammonium chloride, the imine is obtained by evaporating the ethereal solution. Mixed fatty-aromatic ketimines are generally more readily decomposed by water, and their isolation is preferably effected by passing dry hydrogen chloride directly into the ethereal suspension of the magnesium derivative. The free imine is isolated from the hydrochloride so formed in the same manner as that adopted for aromatic ketimines.

Ketimines are generally oils or solids of low m. p. which yield crystalline salts. The hydrochlorides dissolve readily in chloroform, and are decomposed by water into the corresponding ketone and ammonium chloride. The free bases are much less sensitive to the action of water than the salts. Ketimines readily combine with bromine. They yield acyl derivatives which are decomposed by cold dilute hydrochloric acid with the formation of ketones. The constants of the following ketimines are given: *Phenyl ethyl ketimine*,

$$CEtPh:NH,$$
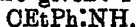
has b. p. 101·5—102·5°/13·5 mm., D_4^{22} 0·9902, n_D^{22} 1·5476. Its *hydrochloride* and *acetyl* derivative have m. p. 145° and 126° respectively. *Phenyl propyl ketimine*, has b. p. 99°/8 mm., D_4^{18} 0·9751, n_D^{18} 1·5353. *Phenyl isobutyl ketimine*, b. p. 113—114°/12·5 mm., D_4^{20} 0·9489, n_4^{2} 1·5270. *Phenyl cyclohexyl ketimine*, b. p. 135—138°/5 mm. *Diphenyl ketimine*, b. p. 127°/3·5 mm., D_4^{19} 1·0847, n_D^{19} 1·6191. *Phenyl o-tolyl ketimine*, b. p. 136—137°/4 mm., $D_4^{19·5}$ 1·0614, $n_D^{23·5}$ 1·6065. *Phenyl p-tolyl ketimine*, m. p. 37°, b. p. 147°/5 mm., D_4^{19} 1·0617, n_D^{20} 1·6097. *Phenyl a-naphthyl ketimine*, m. p. 68—69°, b. p. 181·5°/4·5 mm..   H. W.

Catalytic Formation of Benzophenone by Calcium Carbonate. Paul Sabatier (*Anal. Fis. Quim.*, 1913, **11**, 274—275).— When the vapour of benzoic anhydride is passed over calcium carbonate at about 500°, benzene, benzophenone, and traces of anthraquinone are formed.   G. D. L.

Transformation of 2:6-, 2:4'- and 2:4-Dibromobenzo-phenones into Bromofluorenones. Pieter J. Montagne and Jacob Moll van Charante (*Rec. trav. chim.*, 1913, **32**, 164—173. Compare A., 1910, i, 42).—When 2:6-, 2:4'-, or 2:4-dibromobenzophenone is heated, hydrogen bromide is evolved, and a bromofluorenone formed. Concurrently a certain amount of bromination occurs, due apparently to the hydrogen bromide evolved, and, since different by-products are obtained from 2:4'- and 2:4-dibromobenzophenone, it appears that it is the unchanged original substance which is thus affected.

8-*Bromofluorenone*, $C_6H_3Br \underset{CO}{\diagup}\underset{}{\diagdown} C_6H_4$, m. p. 135°, b. p. ca. 395° (decomp.), is obtained when 2 : 6-dibromobenzophenone is heated at its b. p. during two to three days. On reduction by means of sodium amalgam in boiling alcoholic solution, it is converted into fluorenyl alcohol, m. p. 153°, whilst oxidation by concentrated sulphuric acid and mercuric sulphate transforms it into phthalic anhydride.

When 2 : 4'-dibromobenzophenone is heated, it yields a mixture of unchanged material and two substances which can be separated by sublimation under reduced pressure. At about 170—180°, 6-*bromofluorenone* is obtained. After recrystallisation from benzene, it forms needles and plates, m. p. 165·5°, or compact crystals, m. p. 162·5°. After re-solidification the latter melt at 165·5°. Reduction with sodium amalgam in boiling alcoholic solution transforms it into fluorenone, m. p. 82°, whilst, when oxidised with concentrated sulphuric acid and mercuric sulphate, it yields phthalic anhydride. The residue obtained from the sublimation of 6-bromofluorenone, when sublimed at about 225°, gives a dibromofluorenone, $C_{13}H_6OBr_2$, yellow crystals, m. p. 215·5—216°.

When 2 : 4-dibromobenzophenone is treated in the same manner as the 2 : 4'-isomeride, it yields 6-bromofluorenone. The residue left in the sublimation apparatus, after repeated crystallisations from benzene and alcohol, gives 6 : 8-dibromofluorenone, m. p. 225°. H. W.

αβ-Unsaturated Diketones. OTTO DIELS and PETER SHARKOFF (*Ber.*, 1913, **46**, 1862—1870. Compare A., 1911, i, 464).—Under the influence of 33% aqueous potassium hydroxide, dimethyl diketone monoxime readily condenses with benzaldehyde, cinnamaldehyde and furfuraldehyde, yielding oximes of αβ-unsaturated ketones of the formula $CHR:CH \cdot C(N \cdot OH) \cdot COMe$, from which the corresponding ketones cannot be obtained by any of the usual methods. The removal of the oximino-group may, however, be effected by distilling a mixture of the oxime with phthalic anhydride or succinic anhydride in superheated steam, but the yield of unsaturated diketone thus obtained is very small.

Styryl methyl diketone monoxime, $CHPh:CH \cdot C(N \cdot OH) \cdot COMe$, prepared from benzaldehyde and dimethyl diketone monoxime, crystallises from alcohol in long, colourless needles, m. p. 147° (corr.), and dissolves in aqueous alkali hydroxides, yielding yellow solutions; with 33% potassium hydroxide it forms a *potassium* salt. It is accompanied by an orange-yellow *substance*, probably

$$CHPh[CH_2 \cdot CO \cdot C(N \cdot OH) \cdot CH:CHPh]_2,$$
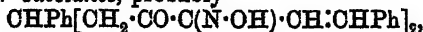
m. p. 216—220° (decomp.).

That the condensation of the aldehyde takes place at the methyl group adjacent to the oximino-group has been established by the conversion of the styryl methyl diketone monoxime by boiling with strong hydrochloric acid into 3-*acetyl*-5-*phenyl*-4 : 5-*dihydroisooxazole*,

$$\underset{O \underline{\qquad} N}{CHPh \cdot CH_2} >C \cdot COMe,$$

which crystallises in stout prisms, m. p. 97—98°, and when warmed with aqueous potassium hydroxide is transformed into a *substance*, m. p. about 254° (decomp.).

On treatment with oxalyl chloride in ethereal solution the oxime yields a *compound*, CHPh:CH·C(COMe):N·O·COCl, which crystallises in colourless needles, m. p. 59°, and is decomposed by water with the formation of cinnamic acid. The *dibromide* of styryl methyl diketone forms yellow crystals, m. p. 86°, and slowly decomposes when kept.

Cinnamylidenediacetyl monoxime (*β-styrylvinyl methyl diketone monoxime*), CHPh:CH·CH:CH·C(N·OH)·COMe, crystallises in slender, yellow needles, m. p. 148°, which become strongly electric when rubbed, give an intense purple-red coloration with sulphuric acid, and on distillation with phthalic anhydride in superheated steam yield *cinnamylidinediacetyl monoxime*, brownish-yellow needles, m. p. 49°.

Furfurylidenediacetyl monoxime (*β-furylvinyl methyl diketone monoxime*), $C_4H_3O·CH:CH·C(N·OH)·COMe$, has m. p. 132°, and with strong aqueous potassium hydroxide yields a *potassium* salt.　　F. B.

Curcumin. VICTOR LAMPE and J. MIŁOBĘDZKA (*Ber.*, 1913, **46**, 2235—2240).—The authors are endeavouring to confirm, by direct synthesis, the formula, $CH_2[CO·CH:CH·C_6H_3(OMe)·OH]_2$, proposed for curcumin by Miłobędzka, Kostanecki, and Lampe (A., 1910, i, 628), and with this object in view have first of all turned their attention to the preparation of the parent substance, dicinnamoylmethane (IV), the synthesis of which was finally accomplished from ethyl cinnamoylacetoacetate by the method indicated in the following scheme :

(I) CHPh:CH·CO·CH(COMe)·CO₂Et →

    (II) CHPh:CH·CO·CH₂·COMe + CHPh:CH·COCl →

(III) COMe·CH CO·CH:CHPh)₂ →

    (IV) CH₂(CO·CH:CHPh)₂ + CH₃·CO₂H.
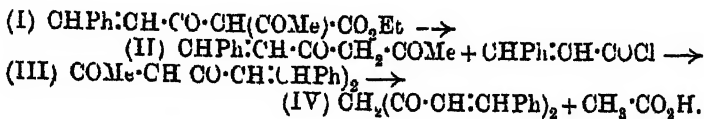
Cinnamoylacetone (II), prepared by hydrolysis and simultaneous elimination of carbon dioxide from ethyl cinnamoylacetoacetate (I), crystallises in yellow prisms, m. p. 86—88°, and develops a yellowish-green coloration with sulphuric acid. Its alcoholic solution gives with copper acetate a green precipitate, and with ferric chloride a deep red coloration. When boiled with hydroxylamine hydrochloride in alcoholic solution, it is converted into 3(or 5) *styryl-*5(or 3)*-methyl-isooxazole*,

    $\overset{CMe:CH}{\underset{O\text{———}N}{}}$>C·CH:CHPh or $\overset{CMe·CH}{\underset{N\text{———}C}{}}$>C:CH:CHPh, which

crystallises in white leaflets, m. p. 92—94°. On successive treatment with sodamide and cinnamoyl chloride in ethereal solution, it yields *dicinnamoylacetone* (III). This has m. p. 112—114°, gives the same reactions as cinnamoylacetone with cupric acetate and ferric chloride, and yields strongly yellow, fluorescent solutions with sulphuric acid.

Dicinnamoylmethane (IV), prepared by boiling dicinnamoylacetone with 50% acetic acid, crystallises in bronze-yellow, prismatic needles, m. p. 144°. In its chemical properties it strongly resembles curcumin. Thus, it dyes cotton a pale yellow without a mordant, dissolves in sulphuric acid, yielding an orange-red solution having a yellow fluor-

escence, and gives with copper acetate and ferric chloride in alcoholic solution a green precipitate and a deep red coloration respectively. When boiled with alcoholic hydroxylamine hydrochloride it is converted into 3 : 5-*distyrylisooxazole*,

$$\underset{N \quad - \quad O}{\overset{CHPh\!:\!CH\cdot C\cdot CH}{\parallel}}\!\!>\!C\cdot CH\!:\!CHPh, \quad crystal-$$

lising in almost colourless, prismatic needles, m. p. 170—172°.

Attempts to prepare ethyl dicinnamoylmalonate by the successive action of sodium and cinnamoyl chloride on ethyl malonate in ethereal solution led to the formation of *ethyl* 4-*cinnamoyl*-1-*phenyl*-Δ^1-*cyclopenten*-3 : 5-*dione*-4-*carboxylate*,

$$\underset{CH - CO}{\overset{CPh\cdot CO}{\parallel}}\!\!>\!C\!\!<\!\underset{CO_2Et}{\overset{CO\cdot CH\!:\!CHPh}{}}, \quad which$$

forms prismatic needles, m. p. 188—189°, and is accompanied by *ethyl* 1-*phenyl*-Δ^1-*cyclopenten*-3 : 5-*dione*-4-*carboxylate*,

$$\underset{CH - CO}{\overset{CPh\cdot CO}{\parallel}}\!\!>\!CH\cdot CO_2Et,$$
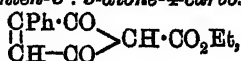
This crystallises in prismatic needles, m. p. 107—109°, and yields deep red alcoholic solutions. F. B.

Diketones Obtained by the Action of Xylylene Dibromides on the Sodium Derivative of Phenyl *iso*Propyl Ketone, and their Decomposition by Sodamide. PH. DUMESNIL (*Compt. rend.*, 1913, **157**, 53—55. Compare A., 1911, i, 719, and Haller and Bauer, A., 1911, i, 726).—o-, m-, and p-Xylylene dibromides react with the sodium derivative of phenyl *iso*propyl ketone in benzene solution to give the corresponding *bis*-(β-*benzoyl*-β-*methylpropyl*)*benzenes*,

$$C_6H_4(CH_2\cdot CMe_2\cdot COPh)_2.$$
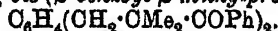
The *ortho*-derivative is obtained as small, colourless crystals, m. p. 68°, giving a *dioxime*, m. p. 240° ; the *meta* in large, colourless crystals, m. p. 44°, giving a *dioxime*, m. p. 210°, and the *para* in colourless needles, m. p. 113°, yielding a *dioxime*, m. p. 278°. All three of these diketones are decomposed, by warming them with sodamide in xylene solution, into the corresponding bis-dimethyl-acetamides. o-*Xylylene-bisdimethylacetamide*,

$$C_6H_4(CH_2\cdot CMe_2\cdot CO\cdot NH_2)_2,$$
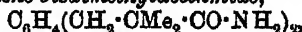
is a colourless, crystalline solid, m. p. 130° ; the *meta*-isomeride, colourless needles, m. p. 162° ; and the *para*-isomeride, m. p. 238°. They are all hydrolysed by heating with 50% sulphuric acid in sealed tubes for six hours at 150° to the corresponding *acids* having respectively m. p.'s 135°, 155°, and 217°. W. G.

Di-iminonaphthol Hydrochlorides. III. OSWALD MILLER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 580—608. Compare A., 1911, i, 308, 465).—When crystallised from water and from alcohol, di-iminonaphthol hydrochloride shows different solubilities in 50% aqueous alcohol. Further, whilst hydration in neutral aqueous solution of the salt obtained from water gives yields of amino-α-naphthaquinone varying regularly with the temperature, the hydrochloride separated from alcohol always yields smaller and inconstant proportions of the quinone owing to the simultaneous formation of a third amino naphthaquinone or β-oximinonaphthol.

From these isomeric di-iminonaphthol hydrochlorides ammonia separates identical bases, but dissociation into base and hydrogen chloride is peculiar to the normal or α-salt; the β'-salt, which does not dissociate, decomposes immediately into β-oximinonaphthol and ammonia.

The decomposition of the hydrochlorides in aqueous solution proceeds normally at temperatures up to about 60°, beyond which the primary products of the reaction yield two secondary products : (1) a dark blue colouring matter, which results from the condensation of α-oximinonaphthol and dissolves in alcohol, giving a blue solution with an intense brick-red fluorescence; it dissolves in varying degree in the products of the reaction, and of the product obtained at 94° it forms about 0·5%. (2) 2-Hydroxy-α-naphthaquinone, which is formed by hydration of the amino-group of aminoquinone, $\cdot NH_2 + H_2O = \cdot ONH_4$. The velocity of this hydration differs for these three quinones, being almost negligible for amino-α-naphthaquinone, only slightly greater for β-oximinonaphthol, and more or less considerable for α-oximinonaphthol. Hence, when the hydration is continued for only ten hours, it may be assumed that the 2-hydroxy-α-naphthaquinone formed is derived entirely from α-oximinonaphthol.

The actual amounts of the three primary products of the reaction are calculated from the equations : (I) amino-α-naphthaquinone $= \alpha + 0·046\alpha + 0·84$; (II) α-oximinonaphthol $= \beta - 0·046\alpha - 4·20 + 0·247$, and (III) β-oximinonaphthol $= \beta' - 0·47\beta'/100 + 4·20$, where α, β, and β' are the experimental quantities of the three products per 100 grams of the hydrochloride.

When crystallised from dilute hydrochloric acid, all the different modifications of the hydrochloride are converted into one and the same form, identical in its decomposition products with that obtained by repeated crystallisation of the crude salt from water. This salt, termed the A-salt, is the one mostly employed in the present investigation.

In the decomposition of the hydrochloride (A-salt) by acid, the yields of amino-α-naphthaquinone and of α-oximinonaphthol obtained are diminished by repeated crystallisation from either water or acid, and the same is the case with the amount of α-oximinonaphthol converted into hydroxynaphthaquinone and colouring matter ; on the other hand, the proportions of β-oximinonaphthol formed gradually increase. By two or three crystallisations from 95% alcohol, the A-salt is transformed into another, which has constant properties and is termed the B-salt. If the conversion of the B-salt into the A-salt by crystallisation from N/10-hydrochloric acid is determined by absorption of the acid by the salt, the inverse change consists in the gradual removal of the acid from the salt under the influence of the solvent. The A-salt must hence contain, not only chemically combined, non-esterifiable acid, but also a certain amount of acid in another form of combination, and capable of esterification by the action of alcohol.

The change produced in the A-salt by crystallisation is also effected by prolonged heating or by remaining over sodium hydroxide.

From these results it appears highly probable that the principal

part in the transformations of di-iminonaphthol hydrochlorides is played by traces of free hydrochloric acid fixed by the crystals on their formation in an acid solution, the maximum and minimum (zero) of such fixation being represented by the A- and B-salts respectively.

The composition of the B-salt having been found to vary with the acidity of the surrounding medium, a C-salt, the acidity of which remains constant, was prepared by suitable heating and crystallisation. When this salt is heated with dilute hydrochloric acid solutions of different concentrations, it is found that the transformation of the B-salt reaches its limiting value with 0·018 mol. of hydrochloric acid per mol. of C-salt, further addition of acid producing no extra increase in the yield of amino-α-naphthaquinone. The amounts of (1) amino-α-naphthaquinone, (2) α-oximinonaphthol, (3) β-oximino-naphthol, and (4) 2-hydroxy-α-naphthaquinone obtained with different concentrations of hydrochloric acid are shown in the form of curves. The second and third curves are approximately straight lines and are therefore in good agreement with the law of mass action. Curve (1), however, rises at first rapidly and then gradually to a limit, its course being closely similar to that of an adsorption curve. It seems, therefore, that when di-iminonaphthol is crystallised from water containing free hydrochloric acid, the latter is adsorbed to some extent on the faces of the crystals. Thus, adsorption in a hetero-geneous system is not limited to substances in a colloidal state, but takes place also with crystalloids.

Further experiments show that in a 1% solution of the B-salt maintained at 94·5°, two processes occur simultaneously : (1) deco m position of the normal A-salt in 0·66% solution, with formation of α- and β-aminonaphthaquinones, and (2) decomposition of the β'-salt, not yet isolated, in 0·33% solution, with formation of β-oximino-naphthol.

β-Oximinonaphthol crystallises in shining, flat, reddish-brown needles having the same composition as the α-compound,

$$C_{10}H_7O_2N,\tfrac{1}{2}H_2O.$$

The two isomeric di-iminonaphthol hydrochlor l s are regarded as having the structures :

(α) $C_6H_4{<}^{CO \cdot C(NH_2)}_{C(:NH_2Cl)-}{>}OH$ and (β) $C_6H_4{<}^{C \cdot \text{------} C:NH_2Cl}_{C(NH_2):CH}$.
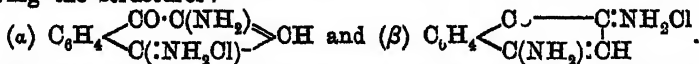
The following salts of di-iminonaphthol have been prepared and analysed : the normal *sulphate*, $(C_{10}H_8ON_2)_2,H_2SO_4,4H_2O$; the *acid acetate*, $C_{10}H_8ON_2,2C_2H_4O_2$, and the normal *acetate*,

$$C_{10}H_8ON_2,C_2H_4O_2,xH_2O.$$

T. H. P.

Lakes. II. PAUL PFEIFFER [and PH. FISCHER, J. KUNTNER, P. MONTI, and Z. PROS] (*Annalen*, 1913, **398**, 137—196. Compare A., 1911, i, 899).—The main object of the paper is to show that in hydroxyketones and hydroxyquinones, particularly of the anthra-quinone series, the formation of normal salts occurs quite differently from that of internally complex salts.

The author has already shown in connexion with his theory of

halochromy (A., 1911, i, 788) that carbonyl compounds and stannic chloride form additive compounds of the type $Cl_4Sn{\cdot}{\cdot}{\cdot}\begin{smallmatrix} O{:}CRR' \\ O{:}CRR'' \end{smallmatrix}$ When the ketone or quinone contains a hydroxyl group in the ortho-position to the carbonyl group, a substituted compound is formed which is represented by the formula $\begin{smallmatrix} RC{=}O \\ | \\ Ar{-}O \end{smallmatrix}{>}SnCl_3$, and is closely related to the tin lakes (*loc. cit.*). The correctness of this view is supported by the following new facts. Acetophenone, benzophenone, xanthone, and *p*-methoxychalkone form with stannic chloride additive compounds of the first type, whilst their *o*-hydroxy-derivatives yield substituted, internally complex salts of the second type. The formation of the substituted compound is preceded by that of the additive compound because in the cases of *o* hydroxyacetophenone, resacetophenone, and benzylidenepaeonol, the additive compound,

$$Cl_4Sn{<}\begin{smallmatrix} O{:}CRAr \\ O{:}CRAr' \end{smallmatrix}$$
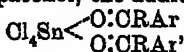
can be isolated; by loss of hydrogen chloride, it changes to the internally complex salt, $\begin{smallmatrix} RC{:}O \\ | \\ Ar{\cdot}O \end{smallmatrix}{>}SnCl_3$. So also, alizarin dimethyl ether and stannic chloride in dry benzene at the ordinary temperature yield $Cl_4Sn{...}OC{<}\begin{smallmatrix} C_6H_4 \\ C_6H_2(OMe)_2 \end{smallmatrix}{>}CO$, which is converted by warming into $Cl_3Sn{<}\begin{smallmatrix} O{:}C{-}C_6H_4 \\ O{\cdot}C_6H_2(OMe) \end{smallmatrix}{>}CO$, methyl chloride being evolved.

The theory that the $SnCl_3$ compounds are internally complex salts containing $Sn{...}O$ is supported by the fact that the colours of these substances are in harmony with the generalisations made with respect to the colours of $SnCl_4$ additive compounds (*loc. cit.*); for example, in the case of resacetophenone derivatives, $OMe{\cdot}C_6H_3{<}\begin{smallmatrix} O{-}SnCl_3 \\ CMe{:}O \end{smallmatrix}$ is colourless, $CHPh{:}CH{\cdot}C{<}\begin{smallmatrix} C_6H_3(OMe){\cdot}O \\ O{\cdots\cdots\cdots}SnCl_3 \end{smallmatrix}$ is orange-yellow, and

$$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C{<}\begin{smallmatrix} C_6H_3(OMe){\cdot}O \\ O{\cdots\cdots\cdots}SnCl_3 \end{smallmatrix}$$
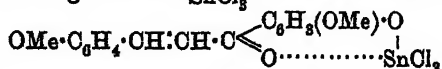
is orange-red. The violet-black colour of the $SnCl_3$ compound of alizarin (and also of alizarin β-methyl ether), in comparison with the red colour of the $SnCl_3$ compound of 1-hydroxyanthraquinone, is in agreement with the rule that in halochromatic substances the presence of a hydroxyl or methoxyl group in the meta-position to the carbonyl group causes a deepening of the colour (*loc. cit.*).

Only *o*-hydroxyketones and *o*-hydroxyquinones yield $SnCl_3$ substituted compounds; the *m*- and *p*-hydroxy-isomerides form $SnCl_4$ additive compounds of the normal type. *o*-, *m*-, and *p*-Hydroxyacetophenones, benzylidenepaeonol (2-hydroxy-4-methoxyphenyl styryl ketone), phenyl *o* hydroxystyryl ketone, 1-, 2- and 4-hydroxyxanthones, and 1- and 2-hydroxyanthraquinones have been examined; of these,

o-hydroxyacetophenone, benzylidenepaeonol, 1-hydroxyxanthone, and 1-hydroxyanthraquinone alone yield $SnCl_3$ substituted compounds. The fact that resacetophenone, resobenzophenone, 2 : 4'-dihydroxy-benzophenone, euxanthone, and alizarin form mono-substituted $SnCl_3$ compounds, not disubstituted $SnCl_2$ compounds, also proves that only the hydroxyl group in the ortho-position to the carbonyl group is concerned in the formation of the internally complex $SnCl_3$ salt.

The $SnCl_3$ derivatives of *o*-hydroxyketones and of *o*-hydroxyquinones, being internally complex salts, must be closely related to the tin lakes of these substances, which are typical representatives of internally complex salts (Tschugaeff, A., 1907, i, 17, 392, 830; Werner, A., 1908. i, 441). On the fibre these lakes do not contain chlorine, and therefore must be derived from the author's compounds simply by replacement of chlorine by oxygen or a hydroxyl group : $C_6H_4\begin{smallmatrix}O-SnCl_3\\ \\CR:O\end{smallmatrix}$

$\longrightarrow C_6H_4\begin{smallmatrix}O-SnO(OH)\\ \\CR:O\end{smallmatrix}$. The author shows that the $SnCl_3$ compounds are converted into tin lakes by hydrolysis. The careful addition of water to the orange solution of the $SnCl_3$ compound of alizarin in pyridine precipitates an orange-red *substance*,

$$(HO)OSn\begin{smallmatrix}O:C-C_6H_4\\ \\O\cdot C_6H_2(OH)\end{smallmatrix}CO,\tfrac{1}{2}C_5NH_5,$$
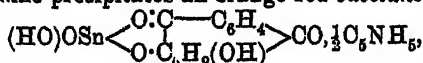
which is unstable to acids, stable to aqueous ammonia on the water-bath, and dyes silk and wool, but not cotton, orange red.

The close relationship between the tin lakes and the author's $SnCl_6$ compounds is also made evident by the following analogy—only hydroxyketones and -quinones containing a hydroxyl group in the ortho-position to the carbonyl group form $SnCl_3$ compounds—only dyes containing a hydroxyl group in the ortho- or peri-position to the chromophoric group are mordant dyes according to Möhlau and Steimming (*Zeitsch. Farb. Text-chem.*, 1904, 3, 358).

According to the preceding, internally complex $SnCl_3$ salts of hydroxy-anthraquinones are obtained by substitution at the ortho-hydroxyl group. Hence it might be anticipated that this hydroxyl group is also concerned in the formation of the normal salts. Experiment shows that this is not so; 1-hydroxyanthraquinone and quinizarin do not form pyridine salts in hot pyridine, whilst 2-hydroxyanthraquinone, 2 : 6-dihydroxyanthraquinone, alizarin. 1 : 7 dihydroxyanthraquinone, and purpurin form pyridine salts, the number of pyridine molecules added being equal to the number of hydroxyl groups in the meta-position to a carbonyl group.

Hence in the formation of normal salts with weak bases just those hydroxyl groups are concerned which do not exhibit any tendency to complex salt formation with tin tetrachloride. Strong bases, such as the hydroxides of the alkali and the alkaline earth metals, react with both *m*- and *o*-hydroxyl groups, but preferably with the former; 2-hydroxyanthraquinone dissolves easily in 1% aqueous sodium carbonate, whilst 1-hydroxyanthraquinone does not.

It follows from the preceding that hydroxyl groups in the ortho-

position to the carbonyl group are concerned in complex salt formation, whilst the production of normal salts is due primarily to hydroxyl groups in the meta-position, normal salt formation at an *o*-hydroxyl group being a secondary effect. This is readily explicable. The hydrogen atom of the *o*-hydroxyl group is attached co-ordinatively to the oxygen atom of the carbonyl group, and therefore its acidic function is weaker than that of the hydrogen atom of the hydroxyl group in the meta-position. Normal salt formation, therefore, occurs firstly at the *m*-hydroxyl group by the addition, in accordance with the modern view of the phenomenon of neutralisation, of the hydroxide, with the formation of an aquo-salt which then loses water.

The compounds obtained by the action of stannic chloride on hydroxy-acetophenones, hydroxychalkones, hydroxybenzophenones, and hydroxy-xanthones are described. The production of a $SnCl_4$ additive compound or of an $SnCl_3$ substituted compound, and also the colours of the products, are quite in accordance with the rules previously stated except in the cases of quinizarin and purpurin which yield the compounds $C_6H_4{<}^{CO}_{CO}{>}C_6H_2{<}^{O}_{O}{>}SnCl_2$ and

$$C_6H_4{<}^{CO}_{CO}{>}C_6H(OH){<}^{O}_{O}{>}SnCl_2$$
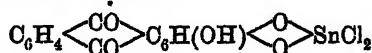
respectively.

The following *substances* have been prepared by warming the carbonyl compound with stannic chloride, alone or in the presence of dry benzene : $OMe \cdot C_6H_3(OSnCl_3) \cdot COMe$, m. p. about 235°, almost colourless leaflets containing $\frac{1}{2}C_6H_6$, from paeonol ;

$$CO_2Me \cdot C_6H_4 \cdot OSnCl_3,$$

m. p. 230°, colourless leaflets, from methyl salicylate ;

$$CO_2Et \cdot C_6H_4 \cdot OSnCl_3,$$
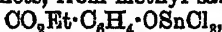
m. p. about 220°, colourless leaflets, from ethyl salicylate ;

$$NH_2 \cdot CO \cdot C_6H_4 \cdot OSnCl_3,$$

m. p. about 260°, white crystals containing $\frac{1}{2}C_6H_6$, from salicylamide ; $OH \cdot C_6H_3(OSnCl_3) \cdot COPh$, m. p. 295—297°, yellow crystals containing $\frac{1}{4}C_6H_6$, from resobenzophenone ; $OMe \cdot C_6H_3(OSnCl_3) \cdot COPh$, m. p. about 262°, yellow crystals, from resobenzophenone methyl ether ; $OH \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot OSnCl_3$, m. p. 294—296°, yellow leaflets, from 2 : 4'-dihydroxybenzophenone ; $C_6H_4{<}^{O}_{CO}{>}C_6H_3 \cdot OSnCl_3$, m. p. 282—284°, yellow crystals containing $\frac{1}{2}C_6H_6$, from 1-hydroxy-xanthone ; $SnCl_4, 2C_6H_4{<}^{O}_{CO}{>}C_6H_3 \cdot OH$, m. p. 239°, yellowish-brown powder, from 2-hydroxyxanthone ; $SnCl_4, C_6H_4{<}^{O}_{CO}{>}C_6H_3 \cdot OH$, m. p. about 230°, yellow crystals, from 4-hydroxyxanthone (m. p. 242°, not 224° as stated in the literature) ;

$$OMe \cdot C_6H_3(OSnCl_3) \cdot CO \cdot CH{:}CHPh,$$
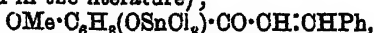
m. p. about 278°, orange-yellow, crystalline powder, from benzylidene-paeonol ; $OMe \cdot C_6H_3(OSnCl_3) \cdot CO \cdot CH{:}CH \cdot C_6H_4 \cdot OMe$, m. p. indefinite at about 250°, orange-red crystals containing $\frac{1}{4}C_6H_6$, from *p*-anisylidene-paeonol ; $OMe \cdot C_6H_3(OSnCl_3) \cdot CO \cdot CH{:}CH \cdot C_6H_3 {:} O_2 {:} CH_2$, decomp. above

200°, orange-red crystals containing $\frac{1}{2}C_6H_6$, from piperonylidenepaeonol ; $C_6H_4{<}{CO \atop CO}{>}C_6H_3{\cdot}OSnCl_3$, brownish-red powder containing $\frac{1}{2}C_6H_6$, from 1-hydroxyanthraquinone ; $C_6H_4{<}{CO \atop CO}{>}C_6H_2(OH){\cdot}OSnCl_3$, violet-black, crystalline powder containing $\frac{1}{4}C_6H_6$, from alizarin ;

$$C_6H_4{<}{CO \atop CO}{>}C_6H_2(OMe){\cdot}OSnCl_3,$$
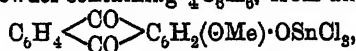
violet-black powder containing $\frac{1}{2}C_6H_6$, from alizarin β-methyl ether ; $C_6H_4{<}{CO \atop CO}{>}C_6H_2{<}{O \atop O}{>}SnCl_2$, red, crystalline powder, from quinizarin ; $C_6H_4{<}{CO \atop CO}{>}C_6H(OH){<}{O \atop O}{>}SnCl_2$, almost black, crystalline powder containing C_6H_6, from purpurin ; $SnCl_4{,}C_6H_4{<}{CO \atop CO}{>}C_6H_2(OMe)_2$, brownish, or golden-yellow leaflets, from alizarin dimethyl ether ; $SnCl_4{,}2C_6H_4{<}{CO \atop CO}{>}C_6H_2(OMe)_2$, m. p. 242°, brownish-orange leaflets, from hystazarin dimethyl ether.

In addition to the normal pyridine salts of the hydroxyanthraquinones previously mentioned, the following have been prepared :

$$CH_3{\cdot}CO{\cdot}C_6H_3(OH)_2{,}C_5NH_5,$$
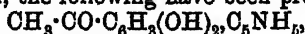
colourless crystals, from resacetophenone ;

$$C_6H_5{\cdot}CO{\cdot}C_6H_3(OH)_2{,}C_5NH_5,$$
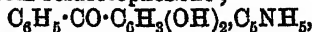
m. p. 58°, colourless plates, from resobenzophenone ;

$$OH{\cdot}C_6H_3{<}{O \atop CO}{>}C_6H_3{\cdot}OH{,}C_5NH_5,$$
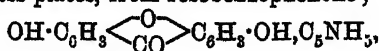
yellow needles, from euxanthone. C. S.

Some Derivatives of Aceanthrenequinone and 1 : 9-Anthracene. M. KARDOS (*Ber.*, 1913, **46**, 2086—2091).—The action of aceanthrenequinone with an equimolecular proportion of hydroxylamine hydrochloride and a half-molecular proportion of sodium carbonate in the presence of alcohol at water-bath temperature, yields *aceanthrenequinoneoxime,*

$$CH{<}{C_6H_4 \atop C_6H_3}{>}\begin{matrix}C{\cdot}CO\\---C{:}NOH\end{matrix} \quad\text{or}\quad CH{<}{C_6H_4 \atop C_6H_3}{>}\begin{matrix}C{\cdot}C{:}NOH\\---CO\end{matrix},$$
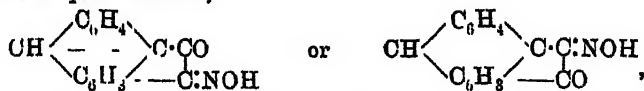
yellow prisms, m. p. 251° (decomp.), which dissolves in sulphuric acid to a brown colour changing to red on warming. When caused to undergo the Beckmann rearrangement, by heating for several hours with hydrogen chloride in acetic acid solution, this substance forms *anthracene-*1 : 9-*dicarboxylimide,* $CH{<}{C_6H_4 \atop C_6H_3}{>}\begin{matrix}C{\cdot}CO\\---CO\end{matrix}{>}NH$, needles, m. p. 293—294°, which is reducible by alkaline reducing agents to a yellow solution, and dissolves in sulphuric acid to a beautiful red solution which fluoresces slightly ; there are obtained simultaneously *anthracene-*1 : 9-*dicarboxylic acid,* which readily passes into its *anhydride,* m. p. 289—290° (*methyl ester,* m. p. 149°), and also *anthracene-*1 : 9-*dicar-*

boxylamic acid, which in the free state rapidly passes into the imide; its solutions in alkali exhibit a beautiful sky-blue fluorescence; the *sodium* and *silver* salts were analysed. Endeavours to methylate the remaining carboxylic group of the acid amide by means of methyl sulphate yielded the *anhydride* of *methyl anthracene*-1:9-*carboxyl-amate*, $CH\underset{C_6H_3}{\overset{C_6H_4}{<}}\underset{CO}{\overset{C\cdot C(OMe)}{>}}N$, or $CH\underset{C_6H_3}{\overset{C_6H_4}{<}}\underset{C(OMe)}{\overset{C\cdot CO}{>}}N$, m. p. 170—171°.
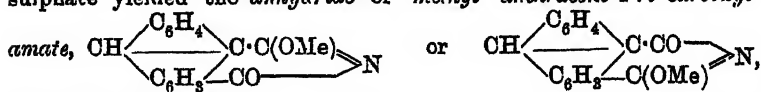
Anthracene-1:9-dicarboxylimide is obtainable in theoretical yield by warming aceanthrenequinoneoxime with sulphuric acid for about a half-hour; heating with potassium hydroxide and a little water at 200—230° converts the imide into a green *dye*, $C_{33}H_{12}O_4N_2$; this on reduction by hyposulphite yields a red vat which colours cotton reddish-violet, passing on exposure to the air to a beautiful green. Similar dyes can be produced from halogen-substituted aceanthrene-quinones.

In an examination of the action of malonyl chloride on anthracene (compare Freund and Fleischer, A., 1910, i, 490; Liebermann and Zsuffa, A., 1911, i, 202) it is found that the condensation product is *anthracene*-1:9-*indandione*, $CH\underset{C_6H_3}{\overset{C_6H_4}{<}}\underset{CO}{\overset{C-CO}{>}}CH_2$, a red powder, m. p. 280° (decomp.) with previous blackening, which in sulphuric acid gives a carmine-red solution with a strong fluorescence; *sodium* salt, red leaflets. On oxidation with alkaline potassium permanganate solution, it produces anthraquinone-1-carboxylic acid. When heated with benzaldehyde at 130°, condensation occurs with formation of the *benzylidene* derivative, $CH\underset{C_6H_3}{\overset{C_6H_4}{<}}\underset{CO}{\overset{C-CO}{>}}C:CHPh$, a brownish-red powder, decomp. at 290°, which gives a reddish-violet solution in sulphuric acid.　　　　　　　　　　　　　　　　D. F. T.
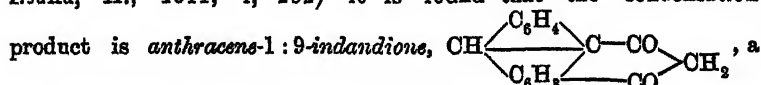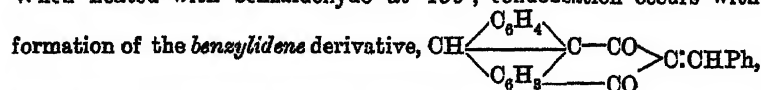
Influence of Constitution on the Rotatory Power of Optically Active Substances. V. Keto-enolic Transformations of Derivatives of Menthyl Acetoacetates. HANS RUPE and EDUARD LENZINGER (*Annalen*, 1913, **398**, 372—378).—*l*-Menthyl *d*-phenylacetoacetate exists in the solid state as the ketonic modification. In benzene it is initially dextrorotatory, but in course of time becomes lævorotatory as the change to the enolic modification proceeds and the *l*-menthyl group becomes the only source of optical activity. It has previously been shown that the rate of transformation is very variable, and been suggested that this variation is caused by the presence of catalysts such as the alkali in the glass vessel. This hypothesis has now been proved. A 9·958% solution, D_4^{20} 0·8891, of *l*-menthyl *d*-phenyl-acetoacetate in benzene containing a trace of piperidine had $[a]_D^{20} + 26\cdot09°$ initially and a final constant value, $[a]_D^{20} - 67\cdot20°$ after ten hours. A similar solution ($c = 10\cdot02$, $D = 0\cdot8895$) containing a drop of piperidine

had initially $[a]_D^{20}$ +26·23°, and a final constant value, – 67·09°, after eight minutes. Within certain limits, the velocity of the keto-enolic change is a function of the concentration of the catalyst.

l-Menthyl *d*-benzoylphenylacetate exhibits a constant rotation in benzene ; also, its alcoholic solution does not develop a coloration with ferric chloride. Hence the stability of the ketonic modification is greatly increased when the methyl group in menthyl phenylacetoacetate is replaced by a phenyl group. However, again the presence of a trace of piperidine increases the velocity of the change from the ketonic to the enolic modification because a solution ($c = 9·08$, D_4^{20} 0·8924) of *l*-menthyl *d*-benzoylphenylacetate in benzene containing a trace of piperidine has $[a]_D^{20}$ +20·76° initially and – 62·83° after eighteen hours.   C. S.

Cardol. LEOPOLD SPIEGEL and M. CORELL (*Ber. Deut. pharm. Ges.*, 1913, **23**, 356—378. Compare Spiegel and Dobrin, A., 1896, i, 653). —Cardol can be distilled in superheated steam or under reduced pressure. In the latter case the principal fraction has b. p. 190°/3 mm., but is of variable composition, as shown by the analysis of two specimens. It is named apo*cardol*, and its reactions with bromine, ozone, permanganate, nitric acid, and on distillation with zinc dust are described. In most cases these do not lead to well-defined products, but the zinc dust distillation yielded ethylene, propylene, 1 : 3-butadiene, and a *substance*, $C_{13}H_{12}O$, m. p. 10°, b. p. 98—100°/14 mm.

In addition to *apocardol* a fraction, b. p. 200—220°/2—5 mm., is obtained.   T. A. H.

Constituents of Ethereal Oils. Eudesmol and its Derivatives. Globulol. FRIEDRICH W. SEMMLER and ERNST TOBIAS (*Ber.*, 1913, **46**, 2026—2032).—The authors have carried out a series of experiments on the sesquiterpene alcohols, eudesmol, which is widely distributed in eucalyptus oils, and globulol, which occurs in the ethereal oil from *Eucalyptus Globulus*. The former has been investigated by Baker and Smith, who consider it to be an oxide having the formula $C_{10}H_{18}O$, and describe a dinitro-derivative, $C_{10}H_{14}(NO_2)_2O$, and a dibromide, $C_{10}H_{16}OBr_2$. The authors, however, are led to the conclusion that it is a bicyclic sesquiterpene alcohol, $C_{15}H_{26}O$, containing one double bond.

Eudesmol has b. p. 156°/10 mm., D^{20} 0·9884, n_D^{21} 1·516, m. p. 78° (Baker and Smith give m. p. 79—80°), $[a]_D^{20}$ +31°21' in chloroform solution. When boiled with acetic anhydride and sodium acetate, it yields *eudesmol acetate*, $CH_3 \cdot CO_2 \cdot C_{15}H_{25}$, b. p. 165—170°/11 mm., D^{20} 0·9933, n_D^{20} 1·49204, $[a]_D^{20}$ +31°.

Dihydroeudesmol, $C_{15}H_{28}O$, b. p. 155—160°/12·5 mm., m. p. 82°, is obtained when an ethereal solution of eudesmol is reduced by hydrogen in the presence of platinum. When treated with sodium acetate and acetic anhydride, it yields the corresponding *acetate*, b. p. 158—164°/10 mm., D^{20} 0·9776, n_D^{20} 1·4788, $[a]_D^{20}$ +13°, from which dihydroeudesmol is recovered unchanged after saponification with

alcoholic potassium hydroxide. When boiled with absolute formic acid, dihydroeudesmol yields *dihydroeudesmene*, $C_{15}H_{26}$, b. p. 126—130°/10 mm., D^{30} 0·9067, n_D^{20} 1·48762, $[a]_D - 7°$.

Eudesmene, $C_{15}H_{24}$, obtained when eudesmol is heated with 90% formic acid, has b. p. 129—132°/10 mm., D^{20} 0·9204, n_D^{20} 1·50738, $[a]_D^{20} + 49°$, and is thus apparently a member of the sesquiterpenes derived from hydrogenated naphthalenes. It yields a characteristic *dihydrochloride* and *dihydrobromide*. The former, m. p. 79—80°, is obtained either by treatment of eudesmol with a saturated solution of hydrogen chloride in glacial acetic acid or by passing hydrogen chloride into eudesmene dissolved in the same solvent. The hydrocarbon is regenerated when the dihydrochloride is boiled with alcoholic potassium hydroxide. The dihydrobromide, m. p. 104—105°, can be prepared by precisely similar methods, and also gives eudesmene when acted on by alcoholic potassium hydroxide.

When treated with zinc dust, eudesmol gives a small quantity of the hydrocarbon, $C_{15}H_{26}$, but is mainly converted into eudesmene. The latter substance is also obtained when phosphorus pentachloride reacts with eudesmol. Oxidation with ozone or potassium permanganate did not lead to definite results.

Globulol, $C_{15}H_{26}O$ (compare A., 1904, i, 604), has b. p. 283°/755 mm. It differs physically from eudesmol, but, possibly, similar relationships exists between the two alcohols as between borneol and *isoborneol*; otherwise they are chemically different. When treated with dehydrating agents, globulol yields a l-*sesquiterpene*, $C_{15}H_{24}$, b. p. 102—103°/6 mm., 247—248°/748 mm., $[a]_D - 55°48'$, n_D^{20} 1·49287, D^{11} 0·8956, and a d-*sesquiterpene*, $C_{15}H_{24}$, b. p. 265·5—266°/750 mm., $a_D + 58°40'$, n_D^{20} 1·50602, D^{15} 0·9236. The latter is possibly identical with eudesmene.   H. W.

Determination of Constitutions in the Camphene Group.

V. Ossian Aschan (*Annalen*, 1913, **398**, 299—313).—Since Auwers has recently upheld, on refractometric evidence, Wagner's formula for camphene, the author has examined two carefully purified specimens of the hydrocarbon. These have been obtained from American and Grecian turpentines respectively, through the pinene hydrochlorides. Each has been twice recrystallised from methyl alcohol (whereby the m. p. is constant), and finally distilled over sodium in a vacuum. The camphene from American turpentine has b. p. 158—158·5°, m. p. 43—43·5°, $D_4^{7''}$ 0 8486, n_a^0 1·46048, and $[a]_D^{1b} + 17·95°$ in benzene. The camphene from Grecian turpentine has b. p. 157·2—157·9°/742 mm., m. p. 46—47°, $D_4^{7'}$ 0·8446, n_D' 1·45641, and $[a]_D^{20} + 74·55°$ in benzene. The molecular refractions, 43·98 and 43 85 respectively, are in close agreement with the value, 43·91, calculated for the semicyclic formula.

The formula $\begin{matrix} CH_2\cdot CH_2 \\ CO\text{——}O \end{matrix}{>}C(CO_2H)\cdot CMe_2\cdot CO_2H$ previously assigned by the author (A., 1910, i, 710) to the lactone-dicarboxylic acid, m. p. 256°, obtained from dehydrocamphenic acid, is now proved to be incorrect. The lactone-dicarboxylic acid is reduced to *iso*camphoronic

acid by hydriodic acid, b. p. 127—128°, at 170—180°. Since the constitution of *isocamphoronic* acid is

$$CO_2H \cdot CH_2 \cdot CMe_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H,$$
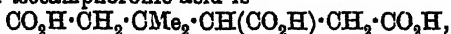
and the lactone-dicarboxylic acid yields formic, succinic, and *iso*butyric acids by fusion with potassium hydroxide, it follows that the hydroxy-acid from which the lactone-dicarboxylic acid is derived must be

$$CO_2H \cdot CH(OH) \cdot CMe_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H.$$
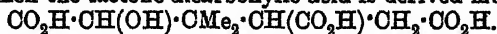
By boiling with hydriodic acid, by heating with 40% hydrogen bromide in glacial acetic acid, or with concentrated sulphuric acid at 100°, or with hydrochloric acid at 170—180°, the lactone-dicarboxylic acid is changed into a stereoisomeric *lactone-dicarboxylic acid*, $C_9H_{12}O_6$, m. p. 185—186°, large prisms. Such stereoisomerism is possible only when at least two side-chains are present attached to different carbon atoms of the lactone ring. Hence the constitutions of the two lactone-dicarboxylic acids are represented by

$$CO_2H \cdot CH_2 \cdot CH \overset{CO\text{---}O}{\underset{CMe_2 \cdot CH \cdot CO_2H}{<}} \cdot$$
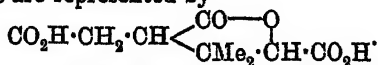
On account of its sparing solubility, the isomeride, m. p. 256°, is regarded as having the trans-configuration.

The author is of opinion that Wagner's formula correctly represents the constitution of camphene. If this is the case, it follows from the preceding work that a transformation must have occurred in the carbon skeleton during the oxidation of camphene by alkaline potassium permanganate.　　　　　　　　　　　　　　　　C. S.

Bornylene and Ethyl Diazoacetate (with a Nomenclature for Tricyclic Carbon Ring Systems). EDUARD BUCHNER and WILHELM WEIGAND (*Ber.*, 1913, **46**, 2108—2117).—The constitution of camphene has recently been demonstrated in a purely chemical manner by the action of ethyl diazoacetate, and the same method is now applied to bornylene (this vol., i, 376). The results indicate that this reagent is of especial value for distinguishing between hemicyclic and endocyclic ethylenic linkings in terpene molecules.

The bornylene applied in this investigation, obtained from borneol through the corresponding methyl xanthate compound, was possibly not quite pure, as its optical activity was somewhat lower than that recorded in the literature; the impurities, however, could not be of such a nature as to affect the trustworthiness of the reaction with ethyl diazoacetate. A solution of ethyl diazoacetate in a little borneol was gradually introduced into a mixture of borneol with a little copper powder at 150°; the reaction is more sluggish than with camphene, but fractional distillation of the product separated *methyl* 4 : 5 : 5-*tri-methyl*tricyclo-[0,1,3 ⁴·⁶, 2]-*octane-2-carb-oxylate* (annexed formula), a colour-less oil, b. p. 136—137°/22 mm., D_4^{21} 1·0283, n_D 1·48337, $[\alpha]_D^{26}$ −8·72°.

$$\begin{array}{l} ^8CH_2 \cdot \overset{6}{C}H\text{---}CH \\ \mid \quad ^5CMe_2 \quad \mid^1 \searrow CH \cdot CO_2Me \\ CH_2 \cdot CMe\text{---}CH \\ ^7 \quad ^4 \quad ^3 \end{array}$$
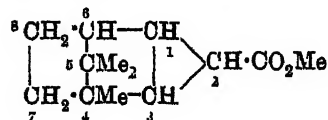
By hydrolysis with alcoholic potassium hydroxide, the corresponding *acid* is obtained, leaflets, m. p. 137°; *calcium, barium, lead,* and *silver* salts, colourless, insoluble substances; *amide,* needles, m. p. 174°.

When the acid is heated with an acid solution of potassium permanganate, oxidation slowly occurs with formation of an oily substance, *trans-cyclo*propane-1 : 2 : 3-tricarboxylic acid, which very gradually crystallised. The identity of this acid was confirmed by the preparation of the silver and calcium salts and of the methyl ester, the m. p., 56—57°, of which was unaffected by admixture with a specimen of synthetic origin. These results are in accord with the annexed usual formula for bornylene.
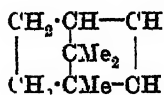
$$CH_2 \cdot CH-CH$$
$$| \quad CMe_2 \quad |$$
$$CH_2 \cdot CMe-CH$$

The paper includes an authorised extension of von Baeyer's scheme of nomenclature for dicyclic systems to tricyclic ones. Each tricyclic system contains two tertiary or quaternary carbon atoms in the ring, which are linked by bridges of carbon chains; these bridges, of which there are four in each tricyclic system, are represented by numbers which represent the number of atoms in each; the grouping of these 4 numbers constitutes the "characteristic"; if these bridges do not extend between the same carbon atoms in each case, the numbers representing the carbon atoms which act as origin and extremity of the bridge must be appended to the corresponding number in the characteristic. The application of this scheme can be seen in the above description of the condensation product of bornylene and ethyl diazoacetate.

D. F. T.

The Synthesis of the Glucosides of the Terpene Alcohols by means of Emulsin. JUHO HAMALÄINEN (*Biochem. Zeitsch.*, 1913, 52, 409—411).—The author has shown (this vol., i, 497, 639) that certain glucosides of the terpene alcohols are readily hydrolysed by emulsin. It seemed therefore possible that synthesis could be effected by the same agency. He has succeeded in obtaining in small quantities synthetically the following glucosides, by allowing the alcoholic solutions of dextrose and the alcohol to react in the presence of emulsin in ethyl alcoholic solutions : *l*-fenchyl-*d*-glucoside, *r-iso*borneol-*d*-glucoside, and *l*-borneol-*d*-glucoside. The formation of these glucosides can explain the action of emulsin in producing glycuronates of terpene-alcohols when injected into animals. A synthetic action of the ferment seems more probable than the formation of an anti-substance, as suggested by various investigators. S. B. S.

Synthesis of β-Geranylglucoside by means of Emulsin; Its Presence in Plants. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1913, 157, 72—74).—β-*Geranylglucoside* is obtained by the action of emulsin on a suspension of dextrose in geraniol saturated with water, or, better, by its action on a solution of the alcohol and sugar in acetone and water. It was separated by the usual method (compare this vol., i, 663), and obtained as a colourless liquid, $[\alpha]_D - 25°49'$, not reducing Fehling's solution, precipitated by basic lead acetate, and rapidly hydrolysed in aqueous solution by emulsin. A glucoside similarly hydrolysed by emulsin to dextrose and geraniol and precipitated by basic lead acetate can be extracted by alcohol from *Pelargonium odoratissimum*. W. G

Cerebronic Acid. III. Its Bearing on the Constitution of Lignoceric Acid. PHŒBUS A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1913, 15, 193—195).—Cerebronic acid yields a normal acid of 24 carbon atoms which is identical with lignoceric acid.   W. D. H.

Azafrin. II. CARL LIEBERMANN and W. SCHILLER (*Ber*, 1913, 46, 1973—1986. Compare A., 1911, i, 391).—Although azafrin and bixin (Hasselt, A., 1911, i, 550) both give blue solutions in concentrated sulphuric acid, they are not identical. This is now shown by the fact that azafrin and methylazafrin give very characteristic colour reactions with a large number of other strong mineral or organic acids, with which bixin gives, at most, only transient and poor effects. One, two, or three molecules of an acid may enter into combination, but the compounds are not simple salts, since azafrin cannot be regenerated from them. Oxidation, reduction, substitution, hydroxyl and ketone reactions have either failed or led to still more complicated substances, but, from the analysis of the above compounds, it seems certain that azafrin has the formula $C_{37}H_{42}O_5$.

It is advisable not be prolong the extraction of azafranillo roots and stems, since benzene dissolves a small amount of a resin which hinders the crystallisation of the desired azafrin. The latter is purified by precipitation from alkaline solution, has m. p. 208°, and yields *methyl-azafrin*, $C_{38}H_{44}O_5$, in sparkling, reddish-yellow leaflets or needles, m. p. 191°, when treated with methyl sulphate. The following *compounds* with acids have been isolated: $B_3,2H_2SO_4$, $B,3HI$, $B,2HBr$, B,HCl, $B,HClO_4$, and $B,3CCl_3·CO_2H$, where B=azafrin or methylazafrin. They are blue or violet in colour, and dissolve in alkalis with never more than partial loss of acid. Phosphoryl chloride, meta-phosphoric acid, and nitric acid also give coloured solutions, but especially characteristic is the reaction with hot anhydrous formic acid, which gives a deep violet solution which may be diluted with water to a stable permanganate-coloured liquid. Glacial acetic acid is a useful indifferent solvent for azafrin, but after boiling the solution for a long time, water precipitates an entirely different substance.

Reduction of azafrin and methylazafrin with zinc dust and acids yields white, amorphous *products*, $C_{31}H_{46}O_4$ and $C_{32}H_{48}O_4$ respectively, whilst hydriodic acid and red phosphorus give rise to compounds which contain phosphorus. Ammonium persulphate yields a white, flocculent acid.   J. C. W.

The Hydrogenation of Pyromucic Acid. HEINRICH WIENHAUS and HERMANN SORGE (*Ber.*, 1913, 46, 1927—1931).—Only in a few cases in the furan group have reductions been effected by hydrogen. The author, in this preliminary announcement, describes tetrahydro-pyromucic acid obtained by the reduction of pyromucic acid with hydrogen and colloidal palladium.

Tetrahydropyromucic acid, $\begin{smallmatrix} CH_2·CH_2 \\ CH_2——O \end{smallmatrix}\!\!>\!CH·CO_2H$, was prepared by adding to the aqueous solution of pyromucic acid a little palladious

chloride solution and gum arabic, and shaking with hydrogen. The acid was purified by distillation, b. p. 131°/14 mm., and then crystallises in rhombohedra, m. p. 21°. It is much more stable than pyromucic acid towards potassium permanganate. The *sodium* salt crystallises in thin tablets; the *potassium, ammonium, barium,* and *silver* salts are all crystalline. When treated with phosphorus trichloride, the free acid is converted into the *chloride,* which reacts with strong ammonia solution, producing the *amide,* leaflets, m. p. 80°, b. p. 135—140°/20 mm. The same amide is formed when the ammonium salt is heated at 200° under pressure.   D. F. T.

A New Chromone Synthesis. ERNST PETSCHEK and HUGO SIMONIS (*Ber.,* 1913, **46,** 2014—2020).—When phenols are condensed with β-ketonic acid esters in presence of sulphuric acid, the products are coumarin derivatives (1 : 2-benzopyrones), but when phosphoric oxide is used, chromones (1 : 4-benzopyrones) are obtained. Ethyl acetoacetate itself has not yet led to definite products, but the method is being extended, particularly with a view to the synthesis of flavone from ethyl benzoylacetate and phenol.

For the preparation of 2 : 3-*dimethylchromone,* $C_6H_4{<}^{O-CMe}_{CO\cdot CMe}$, the dark mass obtained by mixing a solution of dry phenol in ethyl methylacetoacetate with phosphoric oxide is diluted with water, treated with half the quantity of sodium hydroxide required to neutralise the acid, saturated with salt, and extracted with ether. The extract is washed with alkali, dried, and evaporated. The yield is 25%. The compound forms large, transparent, yellow, monoclinic crystals $[a:b:c=1\cdot5201:1:1\cdot5681,\ \beta=73°19\cdot5']$, m. p. 97°. One litre of water dissolves 0·5 gram at 0°, 1·5 grams at 15°, and 4·5 grams at 100°, and the substance is volatile in steam. It forms a *dibromide,* $C_{11}H_{10}O_2Br_2$, in unstable, orange-yellow needles, m. p. 130°, and an *oxime,* $C_{11}H_{10}O:N\cdot OH$, by the direct action of hydroxylamine, in colourless, silky needles, m. p. 158·5°. The isomeric 3 : 4-*dimethylcoumarin oxime,* prepared from 3 : 4-*dimethylthiocoumarin,* m. p. 142°, has m. p. 222°. The oxime of the dimethylchromone yields a *dibromide,* m. p. 180—184°, which readily parts with one molecule of hydrogen bromide to form 2-*bromo-4-nitroso*-2 : 3-*dimethylcoumaran,* $C_6H_4{<}^{C(NO):CMe}_{O-----CBrMe}$, in colourless needles, m. p. 205°.

2 : 3-Dimethylchromone is easily oxidised by permanganate or hydrolysed by 3% sodium hydroxide, yielding salicylic acid. When heated with sodium ethoxide (compare Heywang and Kostanecki, A., 1902, i, 816) it is hydrolysed to *o-hydroxypropiophenone,*

$$OH\cdot C_6H_4\cdot COEt,$$
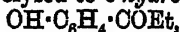
which forms a colourless, mobile, unpleasant smelling oil, b. p. 150°/80 mm. It is sparingly soluble in water, and the solution gives an intense reddish-violet coloration with ferric chloride. The *hydrochloride* of dimethylchromone, $C_6H_4{<}^{O(HCl)\cdot CMe}_{CO----CMe}$, is a white, crystal-

line substance, m. p. 88—92°. On nitration with fuming acid in cold concentrated sulphuric acid, 6-*nitro*-2 . 3-*dimethylchromone*, $NO_2 \cdot C_6H_3 \Big\langle {\overset{O-CMe}{\underset{CO \cdot CMe}{\vphantom{|}}}}$, is obtained in colourless prisms, m. p. 163°, which dissolve in potassium hydroxide with intense yellow colour. The isomeric 6-*nitro*-3 : 4-*dimethylcoumarin*, $C_{11}H_9O_4N$, from 3 : 4-dimethyl-coumarin has m. p. 172°. Both compounds yield 5-nitrosalicylic acid on oxidation. 7(?)-*Chloro*-6-*amino*-2 : 3-*dimethylchromone*, $C_{11}H_{10}O_2NCl$, is obtained when the nitro-compound is reduced by means of tin and hydrochloric acid. It has m. p. 245°, absorbs bromine, and yields a dark red chlorohydroxydimethylchromone.
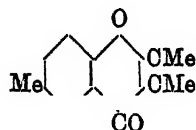
p-Cresol and ethyl methylacetoacetate condense to form 2 : 3 : 6-*trimethylchromone* (annexed formula) in long, colourless, sparkling needles, m. p. 107°, which yield 5-methylsalicylic acid on hydrolysis with dilute alkali. Similarly, *m*-cresol yields 2 : 3 : 7(or 5)-*trimethylchromone*, in clusters of colourless needles, m. p. 96°. The oxidation to a methylsalicylic acid has met with difficulties. J. C. W.

A Simple Process for the Preparation of Flavones. Synthesis of Thioflavone. SIEGFRIED RUHEMANN (*Ber.*, 1913, 46, 2188—2197).—The author has succeeded in condensing β oxyaryl-cinnamic acids to flavones by heating their chlorides with aluminium chloride. Flavones which are substituted in position 8, ortho to the pyrone oxygen, do not show the fluorescence in concentrated sulphuric acid which is characteristic of these compounds in general. In the case of the hydroxyflavones, the removal of the hydroxyl group from the pyrone oxygen is accompanied by a constant depression of the melting point.

The condensation is carried out by adding phosphorus pentachloride to a suspension of the acid in dry benzene and warming until solution takes place, when aluminium chloride is introduced into the product. In this way β-phenoxycinnamic acid (T., 1900, 77, 986) gives an almost theoretical yield of flavone; β-*o*-tolyloxycinnamic acid (*loc. cit.*, 988) forms 8-*methylflavone*, $C_6H_3Me \Big\langle {\overset{CO \cdot CH}{\underset{O-CPh}{\vphantom{|}}}}$, in colourless needles, m. p. 170°, which are gradually decomposed by boiling concentrated potassium hydroxide into acetophenone; β-*m*-tolyloxycinnamic acid (*loc. cit.*, 1120) yields a mixture of 5- and 7-methylflavones; β-*p*-tolyl-oxycinnamic acid (*loc. cit.*, 989) gives 6-*methylflavone*, in colourless needles, m. p. 122—123°, and β-thymoxycinnamic acid (T., 1901, 79, 918) forms 5-*methyl*-8-iso*propylflavone*, $C_{19}H_{18}O_2$, which crystallises in colourless needles, m. p. 143—144°. For the preparation of the isomeride of the latter, ethyl phenylpropiolate was added to a solution of sodium in excess of carvacrol, the resulting yellow, viscous *ethyl β-carvacroxycinnamate*, $C_6H_3MePr \cdot O \cdot CPh:CH \cdot CO_2Et$, b. p. 225°/ 12 mm., was hydrolysed to β-*carvacroxycinnamic acid*, $C_{19}H_{20}O_3$, which formed well-defined, rhombic crystals from light petroleum, and lost carbon dioxide on heating above 103°, and this acid was treated as

above. 8-*Methyl*-5-*isopropylflavone* forms colourless prisms, m. p. 149—150°.

Similarly, β o-methoxyphenoxycinnamic acid (T., 1900, **77**, 1181) was converted into 8-*methoxyflavone*, $C_{16}H_{12}O_3$, which crystallised in colourless, silky needles, m. p. 199—200°, and formed 8-*hydroxy-flavone*, $C_{15}H_{10}O_3$, in colourless needles, m. p. 249—250°, by hydrolysis with concentrated hydriodic acid in a sealed tube. Finally, β-phenylthiolcinnamic acid (*ibid.*) was condensed in the same way to *thioflavone*,

$$C_6H_4 < \begin{matrix} CO \cdot CH \\ S—CPh \end{matrix}, $$ which forms white needles, m. p. 129—130°, and dissolves in warm, concentrated hydrochloric acid. The sulphonium salt and the platinichloride are, however, decomposed by water.

J. C. W.

Thiotetronic Acid and Derivatives. ERICH BENARY (*Ber.*, 1913, **46**, 2103—2107. Compare A., 1910, i, 434, 579).—The results of Anschütz and Bertram (A., 1903, i, 271) suggest that the hitherto unknown thiotetronic acid might be obtained through the interaction of ethyl sodiomalonate and acetylthiolacetyl chloride.

Acetylthiolacetic acid, $SAc \cdot CH_2 \cdot CO_2H$, is obtained by mixing thioglycollic acid and acetyl chloride, when a vigorous reaction ensues; the acid, b. p. 158—159°/17 mm., which can also be obtained by the interaction of thioacetic acid and chloroacetic acid in alkaline solution, gives a deep blue colour with ferric chloride solution, and is converted by phosphorus pentachloride into *acetylthiolacetyl chloride*, a pungent liquid, b. p. 93—95°/20 mm. The chloride cooled in ethereal solution reacts with ethyl sodiocyanoacetate, yielding *ethyl acetylthiol-acetylcyanoacetate* [α-cyano-β-hydroxy-γ-acetylthiol-Δ°-butenoate],

$$SAc \cdot CH_2 \cdot C(OH){:}C(CN) \cdot CO_2Et,$$
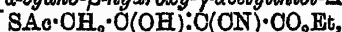
colourless needles, m. p. 70—71°, which indicates its enolic character by a red coloration with ferric chloride and by its acidity. Under similar conditions with ethyl sodioacetoacetate, the *sodium* derivative of *ethyl acetylthiolacetylacetoacetate* is obtained; the free ester is a heavy, yellow oil which passes very readily with elimination of alcohol into α-*acetylthiotetronic acid*, $\begin{matrix} CH_2 \cdot C(OH) \\ S———CO \end{matrix} > C \cdot OAc$, an acidic substance,

needles, m. p. 86—88°; *phenylhydrazone*, yellow needles, m. p. 173—174°, of feeble acid properties. In an analogous manner the interaction of acetylthiolacetyl chloride with ethyl sodiomalonate yields oily *ethyl acetylthiolacetylmalonate*, which on dissolving in sodium hydroxide solution and reprecipitation by acid eliminates a molecule of alcohol with formation of *ethyl thiotetron-α-carboxylate*,

$$\begin{matrix} CH_2 \cdot C(OH) \\ C———CO \end{matrix} > C \cdot CO_2Et,$$ needles, m. p. 122—123°; this reacts acid and gives a blood-red coloration with ferric chloride. On boiling with water for an hour, the ester is converted into *thiotetronic acid*,

$$\begin{matrix} S—CH_2 \\ CO \cdot CH \end{matrix} > C \cdot OH,$$ colourless needles, m. p. 115—117°, which behaves as a monobasic acid and gives a deep red coloration with ferric chloride;

the *silver* salt was prepared. With sodium nitrite, its aqueous solution produces a deep violet coloration. D. F. T.

Isomerism with Diacid Quaternary Ammonium Bases of the Coniine Group. Asymmetric Nitrogen 46. EDGAR WEDEKIND and F. NEY (*Ber.*, 1913, **46**, 1895—1899. Compare Wedekind, A., 1912, i, 509, 948).—Although many investigations have been made, in only one case (E. and O. Wedekind, A., 1910, i, 834) have the two isomeric forms of a diquaternary ammonium salt, in which the nitrogen atoms are asymmetric, been isolated. Endeavours have now been made to effect this isolation of the isomerides by using compounds containing an active asymmetric carbon atom. The addition of menthyl indoacetate to ditertiary bases is not satisfactory. It was found, however, that the aim could be achieved by the application of diacid bases derived from coniine.

*Ethylene-bis-*d-*coniine,*

$$CH_2 \overset{CH_2 \cdot CHPr^a}{\underset{CH_2---CH_2}{<}} N \cdot CH_2 \cdot CH_2 \cdot N \overset{CHPr^a \cdot CH_2}{\underset{CH_2---CH_2}{<}} CH_2,$$
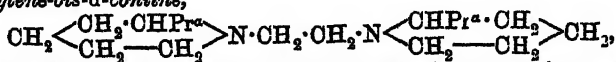
b. p. 200—203°/19 mm., $[a]_D$ +81·09°, obtained by warming together for three hours a mixture of ethylene bromide with a quadrimolecular proportion of *d*-coniine, reacts with benzyl bromide, producing a mixture of diquaternary ammonium salts with an amine-ammonium salt, but the solubility differences in the products are too small to permit separation. With benzyl iodide the chief product, when the reaction occurs unassisted, is the amine-ammonium salt, decomp. at 178°, but if excess of warm molten benzyl iodide is introduced into the warm ditertiary base the product consists mainly of two diquaternary ammonium salts which can be separated by extraction with a mixture of alcohol and acetone; the more soluble and more abundant isomeride (termed *a*-), prisms, decomp. at 130—131°, has $[a]_D$ +40·42°, whilst the β-isomeride, cubical crystals, decomp. at 214°, has $[a]_D$ +15·42°, the solutions in both cases being observed in methyl alcoholic solution.

From theoretical reasons, three isomerides might be expected, represented by the schemes $(N+,C+) \ldots (N+,C+)$, $(N-,C+) \ldots (N-,C+)$, and $(N+,C+) \ldots (N-,C+)$. The *a*- and β-forms isolated are believed to be represented by the first two structures, the isomeride of the third configuration being too unstable to exist under the conditions of the experiment and so passing into the first form. This view is confirmed by the fact that the isomeride of higher rotation, and therefore of the first configuration, preponderates in the reaction product.

*Trimethylene bis-*d-*coniine,* obtained in an analogous manner from coniine and trimethylene bromide, has b. p. 200—201°/17 mm.; unfortunately, its diquaternary salts with benzyl bromide, benzyl iodide, and methyl iodide are amorphous, whilst with allyl iodide the product, which is at first amorphous, on keeping under ether becomes partly crystalline, but very easily undergoes decomposition. That the last substance is the expected *trimethylenebisallylconiinium iodide* was proved by analysis of the corresponding *platinichloride.* D. F. T.

The Behaviour of 2-Methylindole towards Aldehydes and Formic Acid. MAX SCHOLTZ (*Ber.*, 1913, **46**, 2138—2146).—The

interaction of 2-methylindole with aldehydes in alkaline media is strikingly different from its behaviour in acid or neutral solution (Fischer, A., 1887, 265; Freund and Lebach, A., 1905, i, 663).

If equimolecular quantities of 2-methylindole and benzaldehyde are treated with sodium hydroxide solution, a reaction occurs in which the solvent is implicated, for the product is *ethoxyphenyl-2-methylindolyl-methane*, OEt·CHPh·C$\underset{\text{OMe}}{\overset{\text{C}_6\text{H}_4}{<}}$NH, colourless leaflets, m. p. 123°.

A similar reaction with *p*-tolualdehyde in place of benzaldehyde yields *ethoxy-p-tolyl-2-methylindolylmethane*, $C_6H_4Me\cdot CH(OEt)\cdot C_9H_8N$, colourless prisms, m. p. 101°. If methyl alcohol is applied as solvent instead of ethyl, the product is *methoxy-p-tolyl-2-methylindolylmethane*, $C_6H_4Me\cdot CH(OMe)\cdot C_9H_8N$, colourless prisms, m. p. 153°.

Furfuraldehyde, 2-methylindole, and ethyl alcohol under similar conditions yield *ethoxyfuryl-2-methylindolylmethane*,
$$C_4OH_3\cdot CH(OEt)\cdot C_9H_8N,$$
colourless needles, m. p. 158°. With methyl alcohol as solvent, *methoxyfuryl-2-methylindolylmethane*, $C_4OH_3\cdot CH(OMe)\cdot C_9H_8N$, grey prisms, m. p. 108°, is obtained.

The product from anisaldehyde, 2-methylindole, and ethyl alcohol is *ethoxy-p-anisyl - 2 - methylindolylmethane*, $OMe\cdot C_6H_4\cdot CH(OEt)\cdot C_9H_8N$, colourless tablets, m. p. 133°; with methyl alcohol the product is *methoxy-p-anisyl-2-methylindolylmethane*, colourless leaflets, m. p. 151°.

o-Chlorobenzaldehyde, 2-methylindole, and ethyl alcohol yield *ethoxy-o-chlorophenyl-2-methylindolylmethane*, $C_6H_4Cl\cdot CH(OEt)\cdot C_9H_8N$, tablets, m. p. 122°; methyl alcohol gives *methoxy-o-chlorophenyl-2-methyl-indolylmethane*, needles, m. p. 91°.

m-Nitrobenzaldehyde, 2-methylindole, and ethyl alcohol produce *ethoxy-m-nitrophenyl-2-methylindolylmethane*,
$$NO_2\cdot C_6H_4\cdot CH(OEt)\cdot C_9H_8N,$$
yellow leaflets, m. p. 130°; methyl alcohol gives *methoxy-m nitro-phenyl-2-methylindolylmethane*, yellow, rhombic prisms, m. p. 155°.

Nearly all the above products have a tendency to redden if kept in a moist condition.

The behaviour of *o*-nitrobenzaldehyde is curiously abnormal, for, whether methyl or ethyl alcohol is used as solvent, and sodium hydroxide or piperidine as alkali, the one product is *o-nitrophenyl-2-methylindolylcarbinol*, $NO_2\cdot C_6H_4\cdot CH(OH)\cdot C_9H_8N$, orange-red leaflets, m. p. 138°.

Salicylaldehyde also failed to react in the above general manner with methylindole and alcohol, for under the usual conditions the sodium salt of salicylaldehyde is deposited, whilst if water is added to retain this, *o*-hydroxyphenyldi-2-methylindolylmethane (Freund and Lebach, *loc. cit.*) separates. If, however, the mixture of salicyl-aldehyde and methylindole in alcohol is made alkaline by piperidine in place of sodium hydroxide, the piperidine nucleus enters into the reaction product, which is *piperidino-o-hydroxyphenyl-2-indolylmethane*, $C_5H_{10}N\cdot CH(C_6H_4\cdot OH)\cdot C_9H_8N$, colourless prisms, m. p. 201°.

p-Homosalicylaldehyde with piperidine and methylindole in alcoholic solution behaves similarly to salicylaldehyde, producing *piperidino-*

o-*hydroxy-m-tolyl-2-methylindolylmethane*,

$$OH \cdot C_6H_3Me \cdot CH(C_5H_{10}N) \cdot C_9H_8N,$$
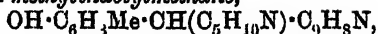
colourless needles, m. p. 132°. These two piperidino-compounds were the only ones obtainable in a crystalline condition, the products from other aldehydes being oily.

That the 3-carbon atom of the pyrrole nucleus is not entirely deprived of its activity in alkaline media is evidenced by the occasional occurrence of traces of di-indolyl derivatives in the reaction product; indeed, with *p*-hydroxybenzaldehyde and cinnamaldehyde the products are entirely of this type. The former aldehyde with piperidine and 2-methylindole in alcoholic solution gives rise to *p-hydroxyphenyl-bis-2-methylindolylmethane*, $OH \cdot C_6H_4 \cdot CH(C_9H_8N)_2$, a crystalline powder, m. p. 237°; in a similar manner, by condensation of one molecule of aldehyde with two molecules of 2-methylindole, cinnamaldehyde produces *styryl-bis-2-methylindolylmethane*,

$$CHPh{:}CH \cdot CH(C_9H_8N)_2,$$
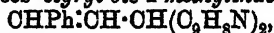
yellow needles, m. p. 226°.

A solution of 2-methylindole in formic acid in a short time becomes deep red, and the addition of water then causes the separation of 2-*methylindolyl-2-methylindolidenemethane*,

$$N{<}^{C_6H_4}_{CMe}{>}C{=}CH{-}C{<}^{C_6H_4}_{CMe}{>}NH,$$
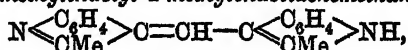
as the *formate*, red needles, m. p. 104°, from which the free *base*, an orange-yellow powder, m. p. 230°, is liberated by ammonium hydroxide; *hydrochloride*; *hydrobromide*, fiery-red needles, m. p. 236°; *perchlorate*, red needles, decomp. at 260°.   D. F. T.

Colours of the Second Order: *holo-* and *meri-*Quinonoid Salts. JEAN PICCARD (*Ber.*, 1913, 46, 1843—1860).—The author has systematically examined the *holo-* and *meri-*quinonoid salts derived from a number of *N*-methyl- and *N*-phenyl-substituted benzidines and *p*-phenylenediamines, and comes to the conclusion that Nietzki's well known rule connecting the increase in the complexity of the molecule with the deepening of the colour from yellow through red and blue to yellowish-green requires modification.

Whereas the *meri-*quinonoid salts derived from benzidine and its diphenyl derivative are coloured respectively blue and yellowish-green, the *meri-*quinonoid salts of tetraphenylbenzidine are yellow.

The author explains this apparent exception as follows: When the complexity of the molecule has been gradually increased to such an extent that the colour has passed successively from yellow to red, blue, bluish-green, and finally yellowish-green, the further increase in the complexity causes a repetition of these colours in the same order; and from analogy with the interference colours the second series are termed colours of the second order.

The *meri-*quinonoid salts of tetraphenylbenzidine thus have a yellow colour of the second order.

Aqueous solution of *meri-*benzoquinonephenyldi-imonium salts are formed by the oxidation of *p*-aminodiphenylamine. The salts are bluish-red and are very unstable, decomposing rapidly in concentrated solution

with the formation of emeraldine. The yellow *holo*-quinonoid salts are still less stable.

Solutions of meri-*benzoquinonephenyldimethyldi-imonium* salts are obtained by oxidising *p*-dimethylaminodiphenylamine in acetic acid solution by means of ferric sulphate. They have a blue colour, whilst those of the *holo*-quinonoid salts are red or reddish-yellow according as they are formed by the union of the base with one or two molecules of the acid ; a blue *ferricyanide* was prepared by methods similar to those employed by Willstätter and Kalb (A., 1908, i, 475).

Benzoquinonediphenyldi-imine (Bandrowski, A., 1888, 269) combines with NN'-diphenyl-*p*-phenylenediamine· to form a quinhydrone *base*, crystallising in yellow leaflets, m. p. 130—135° ; the *holo*-quinonoid salts give red solutions, the *meri*-quinonoid salts greenish-blue ; the *holo*-quinonoid *picrate*, $C_{18}H_{14}N_2,C_6H_8O_7N_8$, forms dark red prisms, the *meri*-quinonoid *picrate*, $C_{86}H_{80}N_4,2C_6H_8O_7N_8$, long, green needles.

Solutions of the *meri*-quinonoid salts derived from tetraphenyl *p*-phenylenediamine are green, whilst those of the *holo*-quinonoid salts are blue ; the salts were not isolated.

On account of their instability. *holo*-diphenoquinonedi-imonium salts, which are yellow in colour, have hitherto not been isolated (compare Willstätter and Kalb, A., 1908, i, 986) ; the *picrate*,

$$C_{12}H_{10}N_2,2C_6H_8O_7N_3,$$
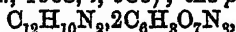
is obtained in pointed, brownish-yellow needles by oxidising benzidine dissolved in glacial acetic acid with aqueous chromium trioxide, and adding picric acid to the resulting solution.

The *holo*-quinonoid base derived from diphenylbenzidine is precipitated in an impure condition by the addition of sodium carbonate to aqueous solutions of the salts, which have been described by Kehrmann and Micewicz (A., 1912, i, 1020).

The green *holo*-quinonoid and yellow *meri*-quinonoid salts derived from tetraphenylbenzidine are obtained by oxidising the base with the requisite amount of chromium trioxide in glacial acetic acid solution ; addition of water and picric acid to these solutions precipitates a very unstable green holo- and a yellow meri-*diphenoquinone-tetraphenyldi-imonium picrate*,

$$C_6H_2O_7N\cdot NPh_2\text{:}C_6H_4\text{:}C_6H_4\text{:}NPh_2\cdot C_6H_2O_7N$$
$$NPh_2\cdot C_6H_5\cdot C_6H_5\cdot NPh_2$$
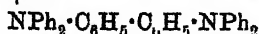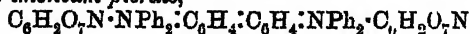
which crystallises in prisms, m. p. 130—134°.   F. B.

holo- and *meri*-Quinonoid Salts of Benzidine. JEAN PICCARD (*Ber.*, 1913, **46**, 1860—1862).—A reply to Madelung (A., 1911, i, 678). The author maintains that the *holo*-quinonoid salts of benzidine are yellow and not blue or violet as stated by Madelung.   F. B.

Hippenyl *iso*Cyanate [Benzoylaminomethylcarbimide]. THEODOR CURTIUS (*J. pr. Chem.*, 1913, [ii], **87**, 513—541).—A recapitulation and extension of earlier work (A., 1896, i, 36) The dibromide of phenylcarbimide, $NPhBr_2\text{:}CO$, which has been previously obtained in an impure condition by boiling benzoylazoimide with bromine in chloroform solution, is prepared by the direct union of bromine and

phenylcarbimide in chloroform solution at a low temperature. It has m. p. 144°, and if carefully heated sublimes undecomposed. When strongly heated, it loses hydrogen bromide, yielding *p*-bromophenyl-carbimide. Benzoylaminomethylcarbimide, $COPh\cdot NH\cdot CH_2\cdot N\text{:}CO$, prepared by heating hippurylazoimide in benzene, chloroform, or carbon tetrachloride solution, has m. p. 96—98° according to the rapidity of heating, combines with methyl and ethyl alcohols to form the urethanes previously described (*loc. cit.*), and when boiled with water yields *s*-dibenzoylaminodimethylcarbamide together with a *substance*, m. p. 130°. It combines with benzamide to form *s*-*benzoylamino-methylbenzoylcarbamide*, $COPh\cdot NH\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot COPh$, which has m. p. 221°, and has also been obtained by heating hippurylazo imide with benzamide in xylene solution.

p-*Bromohippurylazoimide*, prepared from p-*bromohippurylhydrazide* (needles, m. p. 226°) in a similar manner to that employed in the preparation of hippurylazoimide from hippurylhydrazide, crystallises in long, lustrous, silky needles, m. p. 98°, and is converted by boiling in benzene solution into p-*bromobenzoylaminomethylcarbimide*, $C_6H_4Br\cdot CO\cdot NH\cdot CH_2\cdot N\text{:}CO$, which crystallises in broad needles, m. p. 114°, unites with hydrogen chloride in benzene solution yielding a *hydrochloride*, m. p. 235° with previous sintering, and combines with ethyl and methyl alcohols to form the corresponding *urethanes* of m. p. 174° and 214° respectively.

When boiled with water, benzoylazoimide yields only carbanilide, whilst hippurylazoimide gives rise to the following products : carbon dioxide, nitrogen, formaldehyde, hydrazoic acid and its ammonium salt, benzamide, benzoic acid, methylenediamine, ammonium hydrogen hippurate, *s*-dibenzoylaminodimethylcarbamide, and *s*-*benzoylhippuryl-methylenediamine*, $COPh\cdot NH\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot COPh$, which crystallises in slender, silky needles, m. p. 234°, and is hydrolysed by boiling dilute sulphuric acid to benzoic acid, glycine, ammonia and formaldehyde In aqueous alcoholic solution, the decomposition of hippurylazoimide is much simpler, the sole products being dibenzoyl-aminodimethylcarbamide and the urethane,

$$COPh\cdot NH\cdot CH_2\cdot NH_2\cdot CO_2Et.$$
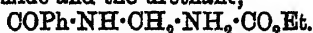
When boiled with water, *p*-bromohippurylazoimide yields di-*p*-bromo-benzoylaminodimethylcarbamide (Heil, *Diss, Heidelberg*, 1911), hydrazoic acid and its ammonium salt, formaldehyde, *p*-bromobenzamide, and *p*-bromohippuric acid. F. B.

Benzoylhydrazicarbonyl. OTTO DIELS and HARUKICHI OKADA (*Ber.*, 1913, **46**, 1870—1876. Compare A., 1912, i, 511, 918).— Benzoylhydrazicarbonyl reacts with acid chlorides, yielding compounds which are undoubtedly derivatives of the type

$$CO<\begin{smallmatrix} N\cdot COPh \\ N\cdot R \end{smallmatrix},$$
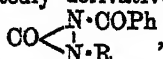
although the formation of metallic salts is best represented on the assumption that the hydrazi-compound has the tautomeric formula
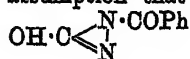
$OH\cdot C<\begin{smallmatrix} N\cdot COPh \\ N \end{smallmatrix}$. Thus, with benzoyl chloride and aqueous potassium

hydroxide it yields dibenzoylhydrazicarbonyl (Stollé and Krauch, this vol , i, 97), which is hydrolysed by fuming hydrochloric acid to benzoic acid and benzoylhydrazicarbonyl, and by dilute sodium hydroxide to *s-dibenzoylhydrazide,* crystallising in lustrous, white needles, m. p. 238°.

Ethyl benzoylhydrazicarbonylcarboxylate, $CO<^{N \cdot COPh}_{N \cdot CO_2Et}$, prepared from benzoylhydrazicarbonyl and ethyl chloroformate, forms colourless crystals, m. p. 94°, and is hydrolysed by warm aqueous sodium hydroxide to *ethyl benzoylhydrazinecarboxylate,* $NHBz \cdot NH \cdot CO_2Et$, which forms lustrous, white plates, m. p. 127°.

On nitration with sulphuric acid and ethyl nitrate, benzoylhydrazicarbonyl is converted into p-*nitrobenzoylhydrazicarbonyl.* This crystallises in pale yellow leaflets, m p. 248°, and is reduced by zinc dust and formic acid to p-*aminobenzoylhydrazicarbonyl,* which forms lustrous, silky, colourless leaflets, m. p. 144°, and yields a *sulphate* (decomp. 238°), *hydrochloride,* and *nitrate.* The amino-compound is decomposed by fuming hydrochloric acid at 130° into aniline and hydrazine hydrochloride, and when heated with hydrazine hydrate is transformed into p-*aminobenzoylcarbohydrazide,*

$$NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot NH \cdot CO \cdot NH \cdot NH_2,$$
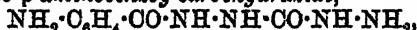
which crystallises from water in lustrous, white leaflets (decomp. 198°), is hydrolysed by hydrochloric acid to *p* aminobenzoic acid and carbohydrazide, and may also be obtained directly from *p*-nitrobenzoylhydrazicarbonyl by the action of hydrazine hydrate at 80°.

<div align="right">F. B.</div>

Constitution of Benzoylhydrazicarbonyl. ROBERT STOLLÉ (*Ber ,* 1913, **46**, 1993—1994).—The reactions of dibenzoylhydrazicarbonyl (this vol., i, 97) agree with either the hydrazicarbonyl formula (I), which has been assigned by Diels and Okada to benzoylhydrazicarbonyl (preceding abstract), or with the dihydro-oxadiazole formula (II).

$$(I) \quad CO<^{NBz}_{NBz} \qquad (II) \quad {}^{NBz \cdot N}_{CO—O}>CPh.$$
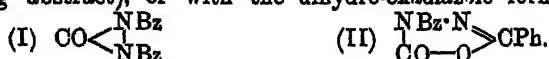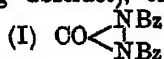
The author proposes to combine nitrobenzoylhydrazicarbonyl with benzoyl chloride and benzoylhydrazicarbonyl with nitrobenzoyl chloride, when the compounds should be identical if formula (I) is correct

<div align="right">J. C. W.</div>

New Series of *iso*Pyrazolones. GEORGES FAVREL (*Compt. rend.,* 1913, **156**, 1912—1914).—It has been shown previously that the γ-chloroacetoacetates react with diazo-chlorides to give the α-alkylhydrazones of γ-chloro-αβ diketobutyrates (A., 1907, i, 796). The latter are now shown to be converted by the action of aqueous solution of sodium hydroxide into alkyl*iso*pyrazolonecarboxylates.

Ethyl phenyliso pyrazolonecarboxylate, $NPh<^{N = C \cdot CO_2Et}_{CH_2 \cdot CO}$, m. p. 258—260°, obtained by the action of aqueous sodium hydroxide solution on the α-phenylhydrazone of ethyl γ-chloro-αβ-diketo-

butyrate, $CH_2Cl\cdot CO\cdot C(N_2HPh)\cdot CO_2Et$, crystallises in long, brilliant, faintly yellow needles from boiling alcohol. The *methyl* ester, m. p. 85—87°, forms small, colourless needles.

*Ethyl o-tolyl*isopyrazolonecarboxylate, m. p. 66—68°, forms feebly yellow crystals with difficulty from alcohol. The *methyl* ester, m. p. 178°, forms whitish crystals soluble in methyl alcohol.

*Ethyl p-tolyl*isopyrazolonecarboxylate, m. p. 111—112°, forms yellow needles, and the *methyl* ester is a crystalline, yellow powder, m. p. 218—220°. All these products in alcoholic solution give intense blue colorations with ferric chloride, which are dissipated by acids. They are soluble in weakly alkaline or strongly acid, but not in dilute acid, solutions. T. A. H.

The Benzoylation of Iminazole [Glyoxaline] Derivatives. OTTO GERNGROSS (*Ber.*, 1913, **46**, 1908—1913).—The author finds that the introduction of acyl groups into iminazole and its homologues, which has hitherto been found impossible, can be affected by mixing the acyl chloride with a bimolecular proportion of the base in ether or benzene solution and shaking for a day or so. The hydrogen chloride formed separates in combination with the excess of base and the acylation proceeds smoothly. If necessary the excess of base can frequently be replaced by the corresponding quantity of pyridine. The benzoyl derivatives are very unstable, and in the course of the preparation great care must be taken for the exclusion of traces of moisture.

1-*Benzoylglyoxaline*, $\begin{smallmatrix} CH:CH \\ N=CH \end{smallmatrix}$>NBz, obtained by evaporation of the benzene solution after the above procedure, slowly crystallises in colourless needles, m. p. 19—20°; when exposed to the air it is rapidly converted by moisture into glyoxaline benzoate, plates, m. p. 99·5°.

1-*Benzoyl*-4(5)-*methylglyoxaline*, obtained in a similar manner, forms needles, m. p. 54—55°; when treated in alcoholic solution successively with silver nitrate and ammonium hydroxide solutions, a *substance* crystallising in needles is precipitated. On exposure to the atmosphere, the benzoyl compound is gradually converted into 4(5)-methylglyoxaline benzoate, plates, m. p. 92—93°.

1-*Benzoyl*-4 : 5-*dimethylglyoxaline*, prepared similarly, forms hexagonal plates, m. p. 74—75°. It is affected by the atmosphere.

Ethyl 1-*benzoyl*-4(5)-*methylglyoxaline*-5(4)-*carboxylate* forms needles, m. p. 43—45°.

1-Benzoylbenziminazole is obtainable in a similar manner to the previous compounds. Although the simultaneously produced benziminazole hydrochloride can be quantitatively re-converted into the original base, if it is preferred the excess of benziminazole can be replaced by pyridine. The benzoyl derivative is more stable than the preceding ones, for although it is hydrolysed by potassium hydroxide solution, it resists sodium carbonate; it gives a *benzoate*, prisms, m. p. 100°, when mixed in ethereal solution with benzoic acid. The precipitate observed by Bamberger and Berlé (A., 1892, 632) in the action of potassium hydroxide on the benzoyl compound was due to the presence of the alcoholate of 1 : 3-dibenzoylbenziminazole as impurity.

Benziminazole can be converted into 1-acetylbenziminazole (Bistrzycki and Przeworski, this vol., i, 103) in the same manner.

<div align="right">.   D. F. T.</div>

The Mechanism of the Scission of Iminazole [Glyoxaline] Derivatives by Benzoyl Chloride and Alkali. OTTO GERNGROSS (*Ber.*, 1913, **46**, 1913—1924).—The action of benzoyl chloride and an alkali hydroxide on glyoxaline, benziminazole, and their homologues in which the imino-group is unsubstituted, even at 0°, causes scission of the ring with formation of an aliphatic acid and a dibenzoylated diamine (Bamberger and Berlé, A., 1892, 632). If sodium carbonate is used in place of the hydroxide with benzoyl chloride and benzimin-azole, a formyldibenzoyl-*o*-phenylenediamine can be obtained, and with benzoyl chloride and water in solution in a mixture of benzene and ether, benziminazole gives a dibenzoylbenziminazole-2-ol; these two new products are evidently to be regarded as intermediate steps in the above scission, and the former compound is easily produced from the latter. It is therefore probable that the mechanism of the scission is similar to that of the scission by alkyl haloids and alkali (compare Meldola and Kuntzen, T., 1911, **99**, 1283), namely:

$$\begin{array}{ccc}
\underset{\text{-N}}{\overset{\text{-NBz}}{>}}\text{CH} \longrightarrow C_6H_4\underset{\text{-N}}{\overset{\text{NBz}}{<}}\text{OH} \longrightarrow C_6H_4\underset{\text{NBz}}{\overset{\text{NBz}}{<}}\text{OH·OH} \\
\text{(I.)} \qquad\qquad\qquad \text{(II.)} \qquad\qquad \text{(III.)} \\
\text{Cl} \quad \text{Bz} \qquad\qquad\qquad \downarrow \\
\text{NHBz·C}_6\text{H}_4\text{·NHBz} \longleftarrow \quad \text{NHBz·C}_6\text{H}_4\text{·NBz·COH} \\
\text{(V.)} \qquad\qquad\qquad\qquad\qquad \text{(IV.)}
\end{array}$$
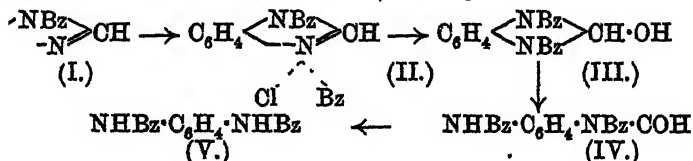
for the last three stages can thus be experimentally realised.

When benzoyl chloride is gradually added to an agitated and cooled aqueous solution of sodium carbonate and 4(5)-methylglyoxaline, a *substance*, tetragonal plates, m. p. 144° (decomp.), probably dibenzoyl-formyl-*αβ*-diaminopropylene, is obtained, which, when boiled with water or treated with cold sodium hydroxide solution, undergoes fission into dibenzoyldiamino-*αβ*-propylene and formic acid.

Experiments devoted to the isolation of the hypothetical additive compound (formula II above) of benzoylbenziminazole and benzoyl chloride were fruitless, the only new product being a small quantity of *benzoylbenziminazole hydrochloride*, needles, m. p. 195—200°, which is converted by alkali hydroxides into benziminazole.

1 : 3-*Dibenzoylbenziminazole-2-ol* (formula III above) is obtained by vigorously shaking for several hours an equimolecular mixture of benzoylbenziminazole and benzoyl chloride with a half-molecular pro-portion of water in a mixture of benzene and ether; the substance crystallises in cubes, and above its m. p., 135—140°, gradually re-solidifies to needles of *formyldibenzoyl-o-phenylenediamine* (formula IV), m. p. 157°; this substance on further heating also solidifies with evolution of carbon monoxide and formation of dibenzoyl-*o*-phenylene-diamine, which finally melts at 306° (decomp.), due to the last stage in the series of changes. The opening of the ring expressed by the formulæ III—IV, which is thus caused by heat, can be effected more readily by merely shaking with cold water or warming with methyl

alcohol. Dibenzoylbenziminazole-2-ol when boiled with alcohol or mixed in the cold with alcohol containing hydrogen chloride or even a little benzoyl chloride is converted into the corresponding *ethyl ether*, $C_6H_4<^{NBz}_{NBz}>OH\cdot OEt$; when heated with propyl alcohol the ethyl radicle is displaced with formation of the propyl ether. Above its m. p., 139°, the ethyl ether undergoes conversion into an *isomeride*, needles, m. p. 152°, which regenerates the original form on mere recrystallisation. In addition to the above-mentioned method, 1 : 3-*dibenzoylbenziminazolol propyl ether*, prisms, m. p. 135—136°, can also be obtained by heating the parent hydroxy-compound with propyl alcohol containing a trace of hydrogen chloride ; in the absence of the hydrogen chloride the iminazole ring is forced open.

The action of benzoyl chloride and sodium carbonate solution on benziminazole yields a mixture of formyldibenzoyl-*o*-phenylenediamine and dibenzoyl-*o*-phenylenediamine, which can be separated by making use of the greater solubility of the former in light petroleum or benzene. The formyldibenzoyl-*o*-phenylenediamine on prolonged boiling with water or more quickly with acids or alkalis is converted into formic acid and dibenzoyl-*o*-phenylenediamine.

It is suggested that the opening of the quinoline and benzothiazole rings by benzoyl chloride and alkali (Reissert, A., 1905, i, 925) may be due to a similar series of changes. D. F. T.

*iso*Hydantoin, 2-Imino-4-ketotetrahydro-oxazole, and its Homologues. WILHELM TRAUBE and RICHARD ASCHER (*Ber.*, 1913, 46, 2077—2084).—The reaction of guanidine with esters of α-amino- and α-hydroxy-acids is more complex than with esters of halogen substituted aliphatic acids (Traube, A., 1911, i, 115), in that not only alcohol but ammonia is eliminated, for example, glycine ester yields glycocyamidine, whilst the esters of the hydroxy-acids yield a reduced oxazole derivative.

When ethyl glycollate is mixed with guanidine in alcoholic solution, heat is developed, and there shortly separates 2-*imino-4-ketotetrahydro-oxazole*, $NH{:}C<^{NH\cdot CO}_{O-CH_2}$, prisms, m. p. 246—247° (decomp.) ; *hydro-chloride*, rhombic tablets, m. p. 164° (decomp.) ; *silver* salt ; *copper* salt, bright blue. The similarity of this substance to ψ-thiohydantoin, for example, in its hydrolysis by alcoholic hydrogen chloride to 2 : 4-*diketo-tetrahydro-oxazole*, $CO<^{NH\cdot CO}_{O-CH_2}$, tablets, m. p. 89—90°, b. p. 173°/11 mm., and by barium hydroxide solution to ammonia, carbon dioxide and glycollic acid, causes the authors to suggest the name ψ- or *iso*-hydantoin for it.

Ethyl lactate also readily reacts with an alcoholic solution of guanidine, giving *methylisohydantoin* (2-*imino-4-keto-5-methyltetrahydro-oxazole*), leaflets, m. p. 226° ; *hydrochloride*, needles. In a manner analogous to the last, this substance undergoes hydrolysis to 2 : 4-*diketo-5-methyltetrahydro-oxazole*, a hygroscopic solid, m. p. 44—45° (decomp.), b. p. 156—161°/15 mm.

By an analogous reaction, ethyl mandelate yields *phenylisohydantoin* (*2-imino-4-keto-5-phenyltetrahydro-oxazole*), crystals, m. p. 256—257° (decomp); *nitrate*, prismatic crystals, decomp. at 133°; this on warming with dilute hydrochloric acid becomes hydrolysed, producing 2 : 4-*diketo-5-phenyltetrahydro-oxazole*, leaflets, m. p. 108°, which is hydrolysed by barium hydroxide solution to mandelic acid, ammonia, and carbon dioxide.

Methyl glycerate reacts readily with guanidine in methyl alcoholic solution, producing *hydroxymethylisohydantoin* (*2-imino-4-keto-5-hydroxy-methyltetrahydro oxazole*), $\mathrm{NH{:}C{<}^{NH\cdot CO}_{\quad O}>CH\cdot CH_2\cdot OH}$, prisms, m.p. 197°.

Ethyl aminoacetate and guanidine react vigorously when mixed in equivalent quantities, yielding glycocyamidine.

Ethyl ethoxyacetate and ethyl ethoxypropionate both readily enter into reaction with a concentrated alcoholic solution of guanidine, yielding *ethoxyacetylguanidine*, m. p. 162°, and *ethoxypropionyl-guanidine*, m. p. 196°, respectively. The formation of these compounds is interesting as an indication of the probable intermediate stage in the formation of the *iso*hydantoin derivatives described above, whilst the absence of the second phase of the condensation serves as a confirmation of the structure assumed for the products obtained from the esters of the hydroxy-acids.   D. F. T.

Syntheses of Thiohydantoin. II. SHIGERU KOMATSU (*Mem. Coll. Sci. Eng. Kyōto*, 1912, **5**, 13—18. Compare A., 1911, i, 683).— The author has modified his interpretation of the mechanism of the reaction whereby thiohydantoin and methylthiohydantoin are formed by the action of potassium thiocyanate on the respective α-amino-acids in the presence of acetic anhydride, and agrees with the view of Johnson and Nicolet (A., 1912, i, 53) that acetyl derivatives of the thiohydantoins are first formed which subsequently undergo hydrolysis. An attempt was made to substitute benzoic anhydride for acetic anhydride, but neither thiohydantoin nor benzoylthiohydantoin was formed.

When potassium thiocyanate and phenyl aminopropionic acid are heated on the water-bath in the presence of acetic anhydride, 2-*thio-3-acetyl-4-benzylhydantoin*, $\mathrm{CH_2Ph\cdot CH{<}^{CO{-}NH}_{NAc\cdot CS}}$, white needles, m. p. 165—166°, is formed, which, when treated with concentrated hydrochloric acid, is converted into 2-*thio-4-benzylhydantoin*, white needles, m. p. 175—177°. Desulphurisation by means of mercuric oxide in ammoniacal solution or by digestion with chloroacetic acid in aqueous solution transforms this into 4-benzylhydantoin, platy crystals, m. p. 185—186°, the *silver* salt of which was analysed (compare Wheeler and Hoffman, A., 1911, i, 498).

Potassium thiocyanate and tyrosine when similarly heated with acetic anhydride yield a viscous, yellowish-brown *acetyl* derivative from which, on hydrolysis, 2-*thio-4*-p-*hydroxybenzylhydantoin*,

$$\mathrm{OH\cdot C_6H_4\cdot CH_2\cdot CH{<}^{CO{-}NH}_{NH\cdot CS}},$$
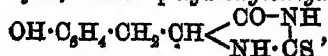
m. p. 203—204° (decomp.), is obtained. Boiling aqueous chloroacetic acid transforms it into 4-*p*-hydroxybenzylhydantoin, m. p. 253—254° (decomp.) [Wheeler and Hoffmann, *loc. cit.*, give m. p. 257—258° (decomp.)].   H. W.

The So called Quinhydrone Salts of the Phenazonium Group. ARTHUR HANTZSCH (*Ber.*, 1913, **46**, 1925—1927).—Mainly polemical in reply to Kehrmann (this vol., i, 298, 522). The author repeats his statement that the former's view as to a quinhydrone structure for the dark green methylphenazonium iodide is incorrect.

As further evidence he cites the neutral character of the solution of this substance, whilst hydrophenazine salts are almost completely hydrolysed by water; the dilute aqueous alcoholic solution of the iodide has the same greenish-yellow colour as the true phenazonium salts; finally, on grinding with silver nitrate solution or with a suspension of silver sulphate in water, the iodide is converted entirely into a greenish-yellow nitrate or sulphate. These salts from their colour cannot be quinhydrone salts, and they contain no admixed dihydrophenazine salts, because otherwise ether would extract the corresponding dihydro-base from them.   D. F. T.

A Condensation Product from Phenylindanone and 1-Phenyl-3-methyl-5-pyrazolone. GEORG ROHDE and M. TENZER (*J. pr. Chem.*, 1913, [u], **87**, 541—544).—With the object of establishing the constitution of the red acid substance produced by the condensation of 1-phenyl-3-methyl-5-pyrazolone with phthalic anhydride (this vol., i, 297), the authors have attempted to prepare a similar compound, but of simpler constitution, by the condensation of the pyrazolone with benzylidenephthalide. The product formed by fusing the two latter compounds in equimolecular proportions is, however, not a carboxylic acid, but a phenyl methylpyrazolonylidenephenylindanone of the following formula:

$$\begin{array}{l} \text{N=CMe} \\ | \qquad \quad \Big\rangle\text{C:C}\Big\langle \dfrac{\text{C}_6\text{H}_4}{\text{CHPh}}\Big\rangle\text{CO,} \\ \text{NPh·CO} \end{array}$$
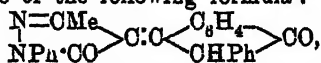
its formation being explained by the transformation of the benzylidenephthalide into 2-phenylindanone, which subsequently condenses with the pyrazolone. This view has been confirmed by the formation of the compound by condensing the pyrazolone with 2-phenylindanone in the presence of anhydrous sodium acetate at 130—135°.

3 : 1'-*Phenyl-3'-methyl-4'-pyrazol-5'-onylidene-2-phenylindanone* crystallises in red needles, m. p. 272°, dissolves in alkalis with a deep magenta coloration, and yields an *oxime* and *semicarbazone*. With sulphuric acid it develops a dark green coloration.   F. B.

Constitution of Anilopyrine. EZIO COMANDUCCI (*Boll. chim. farm.*, 1913, **52**, 436. Compare Comanducci, this vol., i, 296; Zampolli, this vol., i, 296).—Zampolli's criticism is based on errors contained in a preliminary publication of the author, which were corrected before the appearance of Zampolli's paper.   R. V. S.

Iminoindigotins. WALTER MADELUNG (*Ber.*, 1913, **46**, 2259—2264. Compare Binz and Lange, this vol., i, 769).—The mono- and di-imines

can be prepared by heating indigotin with the compound of zinc chloride and ammonia.

The monoimine is obtained in almost quantitative yield by gradually introducing indigotin into the ammonia compound fused at 200°, and maintaining at this temperature for half an hour. In the preparation of the di-imine a higher temperature (about 260°) and more prolonged heating are necessary.

Both imines have the same colour as indigotin, but are much more readily soluble in organic solvents. On reduction with alkaline hyposulphite, the monoimine yields a leuco-compound soluble in alkalis, whilst the di-imine is converted into an insoluble diamine. Advantage is taken of this difference in behaviour to separate the di-imine from the product of the fusion. The leuco-compounds resemble the imines in being readily hydrolysed.

When the monoimine is vatted and the resulting solution, after being heated, submitted to oxidation, a mixture of the monoimine and indigotin is produced. From this the author draws the conclusion that the leuco-compound of the monoimine is present in the vat in the following two forms:

$$C_6H_4{<}^{C(OH)}_{NH}{>}C{\cdot}C{<}^{C(NH_2)}_{NH}{>}C_6H_4 \text{ and }$$

$$C_6H_4{<}^{C(OH)}_{NH}{>}C{\cdot}CH{<}^{C(NH)}_{NH}{>}C_6H_4.$$ The monoimine crystallises with acetic acid (1 mol.).

Di-iminoindigotin, $C_{16}H_{12}N_4$, forms rosettes of microscopic crystals which decompose above 200°, giving off ammonia. It is more readily soluble in all solvents, and possesses more pronounced basic properties than the monoimino-compound. With mineral acids it forms sparingly soluble salts.   F. B.

The Action of Potassium Cyanide on Pyronine and Acridinium Dyes. PAUL EHRLICH and LUDWIG BENDA (*Ber.*, 1913, **46**, 1931—1951).—If the red aqueous solution of pyronine *G* (tetramethyldiaminoxanthylium chloride) is mixed with aqueous potassium cyanide at the ordinary temperature, a violet-red precipitate of tetramethyldiaminoxanthylium cyanide,

$$NMe_2{\cdot}C_6H_3{<}^{CH{-}}_{O(CN)}{>}C_6H_3{\cdot}NMe_2,$$
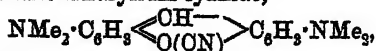
is obtained, which on warming at 65° for ten minutes becomes converted into *tetramethyldiamino-9-cyanoxanthen*,

$$NMe_2{\cdot}C_6H_3{<}^{CH(CN)}_{O{-}}{>}C_6H_3{\cdot}NMe_2,$$
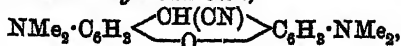
which the authors designate pyronine-leucocyanide (compare Hantzsch and Osswald, A., 1900, i, 256); this substance forms almost colourless needles, m. p. 183°, which rapidly become green when exposed to light; its alcoholic solution on the addition of potassium hydroxide shows a beautiful violet fluorescence. Oxidation of the leuco-compound in hydrochloric acid solution by ferric chloride or lead dioxide, yields *cyano pyronine hydrochloride*, green crystals of metallic lustre; *nitrate*, green, crystalline powder; *chromate*, obtained by effecting the oxidation with dichromate, forms blue flocks; the salts of the base, which has the formula $C_{18}H_{17}ON_3$, give blue aqueous solutions which dye mordanted

cotton and silk, and are reducible to the leuco-compound. With sodium hydroxide solution or ammonium hydroxide in the cold, the salts give a pale blue precipitate, and on acidifying, hydrogen cyanide is evolved, whilst the colour disappears. When boiled with sodium hydroxide solution, complete loss of colour occurs with formation of a precipitate of tetramethyldiaminoxanthone, yellow needles, m. p. 242° (compare Biehringer, A., 1897, i, 73), which in alcohol gives a colourless solution with a violet fluorescence, and in sulphuric acid colourless with a strong blue fluorescence.

If the above tetramethyldiaminoxanthone is reduced by zinc dust and hydrochloric acid in warm aqueous alcoholic solution, *bispyronine,* olive-green crystals, separates as deep blue flocks of a double *salt* with zinc chloride, from which it is freed by dissolving in very dilute hydrochloric acid and salting out. The free base,

$$OCl < ^{C_6H_8(NMe_2)}_{C_6H_8(NMe_2)} > C—C < ^{C_6H_8(NMe_2)}_{C_6H_8(NMe_2)} > OCl,$$
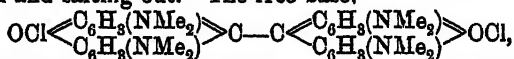
which dissolves in alcohol to a violet solution, and in sulphuric acid to a blood-red, dyes mordanted cotton and silk violet; its violet solution in hydrochloric acid becomes colourless on reduction with zinc dust, but the original coloured substance is regenerated by oxidation with ferric chloride; the base was analysed as the *nitrate.*

3:6-Diamino-10-methylacridinium chloride (compare Benda, A., 1912, i, 651), for which the authors suggest the name *trypaflavin,* when neutralised with sodium carbonate and treated with potassium cyanide in aqueous solution gives an orange-yellow precipitate of the *cyanide*; on warming the mixture at 75°, the precipitate is converted into pale red 3 : 6-*diamino-5-cyano-10-methyldihydroacridine* (compare Kaufmann and Albertini, A., 1909, i, 606), which on oxidation in aqueous hydrochloric acid solution by ferric chloride or potassium dichromate passes into 3 : 6-*diamino-5-cyano-10-methylacridine* (*cyanotrypaflavin*), deep green prisms of metallic lustre which give a magenta-red aqueous solution; the aqueous solution on addition of the required mineral acid precipitates the *nitrate, hydrochloride,* and *sulphate* respectively, which crystallise in needles; the solutions can be reduced by zinc dust and acid to a colourless substance which regenerates the coloured base on oxidation. The hydrochloride suspended in dilute hydrochloric acid is converted by sodium nitrite into a blue *diazo*-compound resembling diazosafranine. If 3 : 6-diamino-5-cyano-10-methyldihydroacridine is warmed for forty hours with sulphuric acid, it is oxidised to 3 : 6-diamino-10-methylacridinium sulphate, together with a *sulphonic acid* of unknown constitution.

When the above diaminocyanomethylacridine is warmed with sodium hydroxide solution, the solution changes its colour from red to brownish-yellow, and 3 : 6-*diamino-10-methylacridone,* colourless needles, when pure, m. p. 308° (decomp.), slowly deposits; this dissolves in hydrochloric acid to a deep yellow solution, and in hot water or alcohol to a colourless solution with a violet fluorescence; the hydrochloric acid solution on diazotisation gives a red *diazo*-compound, which couples with *R*-salt to a sparingly soluble red *substance.* Reduction of diaminomethylacridone with sodium amalgam in alcoholic solution and re-oxidation by ferric chloride in acid

solution produces diaminomethylacridinium chloride in poor yield. Reduction in hydrochloric acid by zinc dust, however, gives the *zinc chloride* double salt, red needles with metallic lustre, of *bistrypaflavin*, $NMeCl \begin{subarray}{l} C_6H_3(NH_2) \\ C_6H_3(NH_2) \end{subarray} > C \cdot C < \begin{subarray}{l} C_6H_3(NH_2) \\ C_6H_3(NH_2) \end{subarray} > NMeCl.$

The formation of this substance is believed to depend merely on the reduction of the pinacone compound which is previously produced (compare Decker and Dunant, A., 1909, i, 433). The addition of nitric acid to a solution of the zincochloride causes the separation of the *nitrate* of the base, orange-red needles; the orange-red aqueous solution of this yields a blue diazo-compound.

3 : 6-Tetramethyldiamino-10-methylacridinium *p*-toluenesulphonate (used in place of the chloride, that is, acridinium-orange, for convenience) reacts with an aqueous solution of potassium cyanide, giving first an orange-red precipitate of the corresponding *cyanide*, which on warming passes into a black green *substance*; this on oxidation in hydrochloric acid solution by ferric chloride gives *cyanoacridinium-orange*, $NMe_2 \cdot C_6H_3 < \begin{subarray}{l} C(CN) \\ NMeCl \end{subarray} > C_6H_3 \cdot NMe_2,$ green crystals soluble in water to a violet colour; *nitrate*, reddish-brown flocks. Reduction of this substance by zinc dust and hydrochloric acid produces a colourless solution, from which oxidation regenerates the original substance as the *chromate* if potassium dichromate is used as oxidising agent. The action of hot potassium hydroxide solution on cyanoacridinium orange causes the formation of *tetramethyldiamino-10-methylacridone*, colourless needles, m. p. 275—276°; *hydrochloride*, yellow needles; the colourless alcoholic solution exhibits a strong violet fluorescence, whilst in sulphuric acid a very strong bluish-green fluorescence is observed. By reduction in dilute hydrochloric acid with zinc dust, tetramethyldiamino-10-methylacridone is converted into *bis-acridinium-orange zincochloride*, red needles with metallic lustre, which, like the previous example, is probably produced by intermediate formation of a pinacone compound; *nitrate*, green crystals with a bronze lustre. The substance is reducible by zinc dust and hydrochloric acid to a yellow solution with green fluorescence, which can be reoxidised to the red solution of the original substance.

Thiopyronine, in an analogous manner, is converted by potassium cyanide into a blue colouring matter.

From a consideration of the colours of the products obtained with potassium cyanide and of the colours of the original pyronine or acridine dye, the conclusion is drawn that the grouping $>$C·CN in orthoquinonoid dyes exerts the same effect as a cyclic nitrogen atom $>$N on the colour; also, that in the cyano-compounds, a rearrangement occurs with formation of a para-quinonoid structure. The latter view is confirmed by experimental results which are to be published later, for example, a striking colour difference exists between 3 : 6-diamino-10-methylacridinium chloride and its 2 : 7-dimethyl derivative, the latter of which is structurally prevented from any such rearrangement.   D. F. T.

Products of the Internal Condensation of Hydrazinedithio-carbophenylamide. MAX BUSCH and WILHELM SCHMIDT (*Ber.*, 1913, **46**, 2240—2248).—The authors have attempted to prepare a derivative of aminocarbodi-imide, $NH:C:N\cdot NH_2$, by the removal of hydrogen sulphide from hydrazinedithiocarbophenylamide (*s*-diphenylthiocarbamylhydrazide), $N_2H_2(CS\cdot NHPh)_2$, by heating with mercuric oxide in alcoholic solution. The product consisted, however, of *tetrahydro-thiodiazoledianil* [*diphenyliminotetrahydrothiodiazole*], $\begin{array}{c}NH\cdot C(NPh)\\NH\cdot C(NPh)\end{array}\!\!>\!S$,
which crystallises in lustrous, white leaflets, m. p. 240°, and can also be obtained, together with the anilinothiolthiodiazole described below, by maintaining the hydrazide in a fused condition for a few minutes at a temperature not exceeding 200°

The thiodiazole has been previously prepared by Walther (A., 1906, i, 831), who assigned to it the formula $NPh:C:N\cdot NH\cdot CS\cdot NHPh$, whilst Freund and Wischewiansky (A., 1894, i, 97), who obtained it by the action of carbonyl chloride on the hydrazide, considered it to be a phenyliminophenylthiourazole of the constitution
$$\begin{array}{c}CS\cdot NPh\\NH\cdot NH\end{array}\!\!>\!C:NPh.$$
Walther's formula is excluded on account of the absence of additive properties, whilst Freund and Wischewiansky's formula is inadmissible because the substance does not possess distinct acid properties and is not oxidisable to a disulphide.
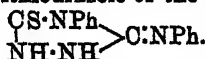
Evidence in support of the authors' formula is furnished by the behaviour of the thiodiazole on oxidation, whereby a red *azo*-compound, *diphenyliminodihydrothiodiazole*, $\begin{array}{c}N\cdot C(NPh)\\N\cdot C(NPh)\end{array}\!\!>\!S$, crystallising in stout, lustrous, dark violet to brownish-red needles, m. p. 113°, is produced. The oxidation is best carried out by heating an alcoholic solution of the thiodiazole with hydrochloric acid and amyl nitrite.

On treatment with nitrous acid the thiodiazole forms a *nitrosoamine*, which is converted by boiling with alcohol or benzene into the above azo-compound. That the sulphur atom of the azo-compound is contained in the ring is proved by its stability towards mercuric oxide, no action taking place even at 140°.

When boiled with concentrated hydrochloric acid. *s*-diphenylthiocarbamylhydrazide loses aniline, yielding *anilinothiolthiodiazole*,
$$\begin{array}{c}N\text{---}N\\C(SH)\cdot S\end{array}\!\!>\!C\cdot NHPh \quad \text{or} \quad \begin{array}{c}N\text{---}NH\\C(SH)\cdot S\end{array}\!\!>\!C:NPh,$$
which crystallises in white needles, and has been previously described by Freund and Imgart (A., 1895, i, 400) as a phenyldithiourazole, $\begin{array}{c}NH\cdot CS\\NH\cdot CS\end{array}\!\!>\!NPh.$
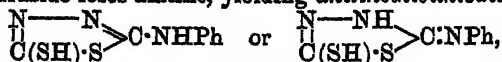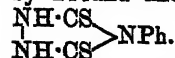
Anilinothiolthiodiazole reacts with methyl iodide and alcoholic potassium hydroxide, yielding *anilinomethylthiolthiodiazole*,
$$\begin{array}{c}N\text{---}N\\C(SMe)\cdot S\end{array}\!\!>\!C\cdot NHPh.$$
This crystallises in lustrous, colourless, glassy needles or large columns,
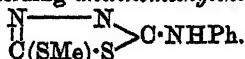
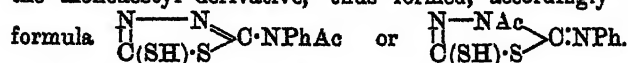m. p. 127°, and has also been obtained by the removal of hydrogen sulphide from methyl thiocarbanilinodithiocarbazinate,

$$SH \cdot C(NPh) \cdot NH \cdot N \vdots C(SH) \cdot SMe.$$
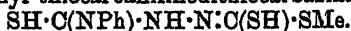
Anilinobenzylthiolthiodiazole, $C_{15}H_{13}N_3S_2$, prepared in a similar manner, using benzyl chloride, forms pale yellow needles, m. p. 141°. That the above alkyl derivatives contain an imino-group has been shown by the preparation of a *nitrosoamine*, $C_9H_8ON_4S_2$, crystallising in needles, m. p. 84—85°, by the action of nitrous acid on the methyl derivative.

When heated at 100° with benzyl chloride and alcoholic potassium hydroxide, the methyl derivative is converted into *benzylanilino-methylthiolthiodiazole*, $C_{16}H_{15}N_3S_2$, which forms transparent prisms, m. p. 85°, and yields a *hydrochloride*, m. p. 169°.

The diacetyl derivative of anilinothiolthiodiazole, m. p. 252°, described by Freund and Imgart (*loc. cit.*), readily loses one of its acetyl groups on crystallisation of alcohol. The acetyl group which is so readily removed must be attached to the sulphur of the atom, and the monoacetyl derivative, thus formed, accordingly receives the

formula $\begin{matrix} N\!\!-\!\!-\!\!N \\ \| \quad\quad \rangle\!C\cdot NPhAc \\ C(SH)\cdot S \end{matrix}$ or $\begin{matrix} N\!\!-\!\!NAc \\ \| \quad\quad \rangle\!C \vdots NPh. \\ C(SH)\cdot S \end{matrix}$

In view of the above results the dithiourazoles described by Freund and Imgart must be considered as amino- or imino-tetrahydrothio-diazoles, whilst the aminothiourazoles are probably di-iminotetrahydro-thiodiazoles.   F. B.

Colour Bases of the Quinoneimide Dyes. I.

FRIEDRICH KEHRMANN, EM. HAVAS, and EUGÈNE GRANDMOUGIN (*Ber.*, 1913, 46, 2131—2138).—An investigation of the quinoneimide colouring matters, which brings to light certain analogies with the triphenylmethane colours. The occurrence of chemical change was detected spectro-scopically.

If a solution of safranine in water is treated with alkali and a layer of ether placed on the surface, the two red layers exhibit quite different absorption spectra; the same difference holds for the two layers in the case of the alkylated safranines, but the colours of the ether-soluble bases are in all cases strikingly similar. As the ammonium bases are insoluble in water, the ethereal solutions must contain the imino-base; on shaking with water partial hydration occurs, and a portion of the imino-base passes from the ether as the azonium base and imparts to the water the colour of the original salt. These azonium bases, which conduct the electric current, precipitate ferric hydroxide from ferric solutions, and are generally more stable than the analogous triphenylmethane bases, can also be obtained by the action of moist silver oxide. The equilibrium $NH_2R + H_2O \longrightarrow NH_3R\cdot OH$ also shows its effect in the action of much potassium hydroxide, when the excess of hydroxyl ion causes practically all the coloured substance to pass into the ethereal layer as the imino-base. To the substance soluble in water is attributed the structure

$$NH_2 \cdot C_6H_3 \begin{matrix} \xrightarrow{\quad\quad N} \\ NPh(OH) \end{matrix} C_6H_3 \cdot NH_2,$$
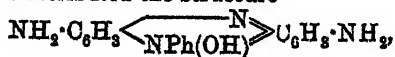
corresponding with the salts, for example,

$$NH_2 \cdot C_6H_3 \diagdown \overset{N}{\underset{NPhCl}{\diagdown}} \diagup C_6H_3 \cdot NH_2,$$
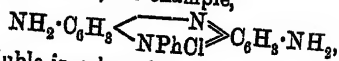
and to the base soluble in e$_t$her either

$$NH_2 \cdot C_6H_3 \diagdown \overset{N}{\underset{NPh}{\diagdown}} \diagup C_6H_3 : NH \text{ or}$$

$$NH_2 \cdot C_6H_3 \diagdown \overset{N}{\underset{NPh}{\diagdown}} \diagup C_6H_3 \cdot NH, \text{ preferably the former as it better}$$
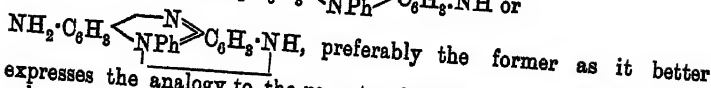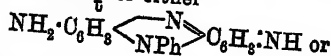
expresses the analogy to the parent substance ammonia in which the valency passes from three to five in salt-formation.

Indamine, the simplest quinoneimide dye, closely resembles safranine in spectrum, thus indicating similarity in constitution, namely, $NH_2 \cdot C_6H_4 \cdot N : C_6H_4 : NH$; when shaken with water, however, it does not undergo any appreciable hydration to the corresponding ammonium base, indicating the less basicity of ammonium nitrogen compared with azonium nitrogen.

Tetraethylsafranine, with dilute potassium hydroxide or moist silver oxide, yields only the azonium base, which is insoluble in ether, but as with crystal-violet, on treatment with concentrated alkali, an ethyl radicle is eliminated with formation of triethylsafranine.

With the thiazine dyes, the introduction of successive methyl groups as with safranine, produces an additive effect in the shifting of the absorption band. Methylene-blue like tetraethylsafranine undergoes scission of one and even two methyl groups under the action of potassium hydroxide. The other ethylated thiazines when treated with alkali yield the ether soluble imino-bases, which on shaking with water pass into the thionium bases with simultaneous assumption of the blue colour characteristic of the salts.

D. F. T.

Bisthiohydantoins. GEORG FREERICHS and H. HÖLLER (*Annalen*, 1913, **398**, 256—264).—*Bisthiohydantoin*,

$$\overset{CH_2 - CO}{\underset{S \cdot C(:NH)}{\diagdown}} N \cdot N \diagup \overset{CO - CH_2}{\underset{C(:NH) \cdot S}{\diagdown}},$$
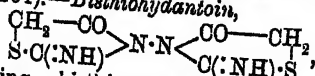
prepared by boiling bisthiocarbamide with aqueous chloroacetic acid, is a colourless, crystalline powder and possesses more pronounced acid properties than thiohydantoin itself. It is easily soluble in alkali hydroxides and carbonates and in aqueous ammonia; the *potassium* salt, $C_6H_6O_2N_4S_2,2KOH$, and *barium* salt, $C_6H_6O_2N_4S_2,Ba(OH)_2$, are crystalline substances. By treatment with methyl or ethyl iodide and $N/2$-potassium hydroxide, an alcoholic solution of bisthiohydantoin is readily converted at the ordinary temperature into NN-*dimethylbisthiohydantoin*, $C_8H_{10}O_2N_4S_2$, m. p. above 270°, colourless needles, or NN-*diethylbisthiohydantoin*, m. p. 224°, neither of which has acidic properties.

Bisthiocarbamide reacts in a similar manner with α-bromopropionic acid and with α-bromobutyric acid. 4 : 4'-*Dimethylbisthiohydantoin*,

$$\overset{CHMe \cdot CO}{\underset{S \cdot C(:NH)}{\diagdown}} N \cdot N \diagup \overset{CO - CHMe}{\underset{C(:NH) \cdot S}{\diagdown}}, \text{ m. p. above 280° (decomp.), forms}$$

a *barium* salt, $C_8H_{10}O_2N_4S_2,Ba(OH)_2$, an NN-*dimethyl* derivative, m. p.

255—256°, and NN-*diethyl* derivative, m. p. 187°.   4 : 4'-*Diethyl-bisthiohydantoin*, m. p. 225—226°, forms a *barium* salt,

$$C_{10}H_{14}O_2N_4S_2,Ba(OH)_2,$$
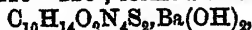
an NN-*dimethyl* derivative, m. p. 216—217°, and NN-*diethyl* derivative, m. p. 154°.   C. S.

The Anomalies of Uric Acid Solubility (Colloidal Uric Acid). HEINRICH SCHADE and E. BODEN (*Zeitsch. physiol. Chem.*, 1913, 86, 238—243. Compare this vol., i, 404).—Polemical in reply to Lichtwitz (this vol., i, 657).   W. D. H.

Action of Hydrazine on the 2 : 4-Dichlorophenylhydrazones of Ethyl α-Chloro- and α-Amino-glyoxylates and the Decomposition of Phenylazoacetoacetamide by Chlorine. Formation of the 2 : 4-Dichlorophenylhydrazone of α-Chloroglyoxylamide and its Basic Derivatives. CARL BÜLOW and PETER NEBER (*Ber.*, 1913, 46, 2032—2045. Compare this vol., i, 207).—The 2 : 4-*dichloro-phenylhydrazone* of α-*hydrazinoglyoxylhydrazide*,

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot NH_2) \cdot CO \cdot NH \cdot NH_2,$$
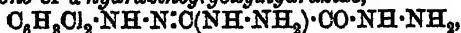
is formed when hydrazine hydrate acts on an alcoholic solution of the 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate under definite conditions which are fully described in the original. It forms straw-yellow leaflets, which rapidly decompose on exposure to air and light, which darken at 155°, and have m. p. 160° (decomp.). It gives an orange-red colour with cold concentrated sulphuric acid which becomes pale, dirty yellow on warming. When warmed with benzaldehyde in alcoholic solution, it yields the corresponding *benzylidine* derivative, $C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot N{:}CHPh) \cdot CO \cdot NH \cdot N{:}CHPh$, yellow needles, m. p. 218° (decomp.).

When an alcoholic solution of the 2 : 4-dichlorophenylhydrazone of ethyl α-aminoglyoxylate is warmed with hydrazine hydrate, the 2 : 4-*dichlorophenylhydrazone* of α-*aminoglyoxylhydrazide*,

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH_2) \cdot CO \cdot NH \cdot NH_2,$$
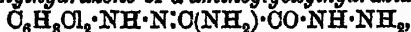
is obtained in long, pale brown needles, m. p. 230° (decomp.). In contrast to the "hydrazidrazone hydrazide" described above, this substance only gives a pale yellow colour with concentrated sulphuric acid, from which the conclusion is drawn that the hydrazino-group attached to the α-carbon atom is the cause of the delicate halochromic property. The presence of the hydrazino-group is established by the preparation of the *benzylidine* derivative,

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH_2) \cdot CO \cdot NH \cdot N{:}CHPh,$$
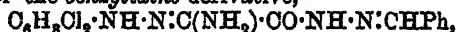
yellow needles.

The 2 : 4-*dichlorophenylhydrazone* of α-*aminoglyoxylacetylhydrazide*, $C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH_2) \cdot CO \cdot NH \cdot NHAc$, is formed when a mixture of the 2 : 4-dichlorophenylhydrazone of ethyl α-aminoglyoxylhydrazide and acetic anhydride is allowed to evaporate at the ordinary temperature. It forms white crystals, m. p. 233°. Its constitution is established by the fact that it does not yield a benzylidine derivative when boiled with benzaldehyde in alcoholic solution, and that it immediately yields a cloudy solution when sodium nitrite solution is added to a solution of it in dilute acid.

An attempt was made to confirm this conclusion in the following manner. The 2 : 4-*dichlorophenylhydrazone* of *ethyl α-acetylaminoglyoxylate*, $C_6H_3Cl_2 \cdot NH \cdot N{:}C(NHAc) \cdot CO_2Et$, white needles, m. p. 153° after previous softening, was prepared by the action of cold acetic anhydride on the 2 : 4-dichlorophenylhydrazone of ethyl α-aminoglyoxylate. When an alcoholic solution of this substance was warmed with hydrazine hydrate, a *product*, $C_{10}H_9ON_5Cl$, white needles, m. p. 205°, was obtained, which yielded a *benzylidene* derivative, and had the formula (1)

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C \cdot N{:}CMe$$
$$\qquad\qquad\qquad CO-N \cdot NH_2, \text{ or}$$

$$(2)\ C_6H_3Cl_2 \cdot N \cdot N{:}C \cdot CO \cdot NH \cdot NH_2$$
$$\qquad\qquad MeC{=}N,$$
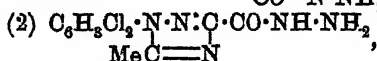
and was formed from the intermediate hydrazide,

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C(NHAc) \cdot CO \cdot NH \cdot NH_2.$$

The 4-*chlorophenylhydrazone* of *ethyl α-aminoglyoxylate*,

$$C_6H_4Cl \cdot NH \cdot N{:}C(NH_2) \cdot CO_2Et,$$
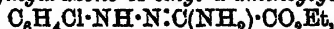
is formed by the action of alcoholic ammonia on the 4-chlorophenyl-hydrazone of ethyl α-chloroglyoxylate (*loc. cit.*). It has m. p. 158°, and can be distilled without decomposition.

The 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate is best obtained by the action of chlorine on a solution of ethyl phenylazo-acetoacetate in acetone. The advantage gained by the substitution of acetone for chloroform (*loc. cit.*) is that the mother liquors from one preparation can be used as solvent for a succeeding preparation, and this procedure has a favourable effect on the yield.

The 2 : 4-*dichlorophenylhydrazone* of *α-chloroglyoxylamide*,

$$C_6H_3Cl_2 \cdot NH \cdot N{:}CCl \cdot CO \cdot NH_2,$$
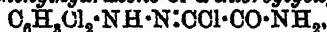
m. p. 232°, is obtained when chlorine is passed into a solution of phenylazoacetoacetamide in glacial acetic acid or alcohol. It is readily soluble in potassium hydroxide. Piperidine converts it into a *substance*, m. p. 136—136·5°, which, at a higher temperature, decomposes suddenly with evolution of a volatile oil. With pyridine, it yields pale flesh-coloured *needles*, m. p. 220—221°. Investigation of these compounds is not completed. The 2 : 4-dichlorophenylhydrazone of ethyl α-amino-glyoxylamide, previously described (*loc. cit.*), is more conveniently obtained by the action of cold alcoholic ammonia on the above amide, and has m. p. 176° instead of 170° as previously given. It forms a *platinichloride*, crystallising in small, yellow octahedra, reduces boiling gold chloride solution, and gives a mirror with cold ammoniacal silver nitrate.

The 2 : 4-*dichlorophenylhydrazone* of *α-hydrazinoglyoxylamide*,

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot NH_2) \cdot CO \cdot NH_2,$$
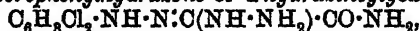
is obtained by the action of hydrazine hydrate on an alcoholic solution of the 2 : 4-dichlorophenylhydrazone of α-chloroglyoxylamide. It has m. p. 157°, and gives an orange coloration with concentrated sulphuric acid. With an alcoholic solution of benzaldehyde, it yields the corresponding *benzylidene* derivative,

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot N{:}CHPh) \cdot CO \cdot NH_2,$$
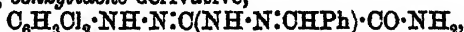
yellow needles, m. p. 205°.

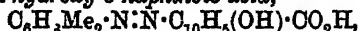In order to determine which of the two amino-groups in the 2 : 4-di-

chlorophenylhydrazone of α-aminoglyoxylamide is more loosely held, this substance was energetically treated with an excess of hydrazine hydrate, when the 2 : 4-dichlorophenylhydrazone of α-aminoglyoxyl-hydrazide was obtained, thus showing the amino-group of the –CONH$_2$ radicle to be the more readily replaceable.   H. W.

Azo-dyes Derived from 2-Hydroxy-3-naphthoic Acid. ANUKUL CHANDRA SIRCAR and EDWIN ROY WATSON (*J. Soc. Chem. Ind.*, 1913, **32**, 642—644).—In a previous paper (A., 1912, i, 1037) the authors have described attempts to prepare dyes similar in constitution to benzeneazosalicylic acid, which would possess the same all-round fastness as this dye, but with the colour deepened to red, violet, blue or black. These attempts were not, however, successful as the colour was deepened towards maroon and brown, instead of towards violet and blue as desired. Since many azo-dyes of not more complicated structure possess the desired shades, the authors have examined a list of the well-known azo-dyes prepared from naphtholsulphonic acids, from which they are led to the conclusion that the relative position of the hydroxyl- and chromophore-group is the determining factor in the colour of the dye, the *ortho*-position favouring red, violet, and blue shades, and the *para*-position giving brown shades. A series of dyes have therefore been prepared by coupling diazonium salts with 2-hydroxy-3-naphthoic acid, the hydroxyl group thus being in the ortho-position to the azo-group. The shades obtained are very satisfactory, including fiery-red, claret, cherry-red, brownish-purple, bluish-purple and black. The dyeings on chrome-mordanted wool are quite satisfactory as regards fastness to light and acid test, but are not so resistant to soaping, alkalis, and milling as they were expected to be.

Naphthalene-α-1-azo-2-hydroxy-3-naphthoic acid, prepared from diazotised α-naphthylamine and 2-hydroxy-3-naphthoic acid, forms greenish-red, rhombic prisms, m. p. 236°, whereas Möhlau and Kriebel (A., 1896, i, 242) gave m. p. about 182°.
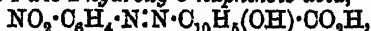
m-*Xylene-1-azo-2-hydroxy-3-naphthoic acid,*
$$C_6H_3Me_2 \cdot N:N \cdot C_{10}H_5(OH) \cdot CO_2H,$$
crystallises in deep red needles, m. p. 240—242°.

p-*Ethoxybenzene-1-azo-2-hydroxy-3-naphthoic acid,*
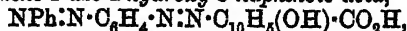$$OEt \cdot C_6H_4 \cdot N:N \cdot C_{10}H_5(OH) \cdot CO_2H,$$
deep red, needle-shaped crystals with green reflex, has m. p. 231° after softening at a somewhat lower temperature.
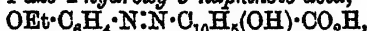
m-*Nitrobenzene-1-azo-2-hydroxy-3-naphthoic acid,*
$$NO_2 \cdot C_6H_4 \cdot N:N \cdot C_{10}H_5(OH) \cdot CO_2H,$$
prepared from diazotised *m*-nitroaniline and 2-hydroxy-3-naphthoic acid, separates from nitrobenzene in beautiful red needles, which do not melt at 275°. The corresponding *dye* from *p*-nitroaniline forms fine hair-like, red needles, which do not melt at 285°.

Benzeneazobenzene-1-azo-2-hydroxy-3-naphthoic acid,
$$NPh:N \cdot C_6H_4 \cdot N:N \cdot C_{10}H_5(OH) \cdot CO_2H,$$
is formed when a diazotised solution of *p*-aminoazobenzene (Hewitt, T., 1909, **95**, 1394) is dropped into an alkaline solution of 2-hydroxy-3-naphthoic acid. It crystallises in magenta-red needles with a green reflex and does not melt below 275°.

Diazotised disulphonaphthalene-β-azo-α-naphthylamine combines with an alkaline solution of 2-hydroxy-3-naphthoic acid to yield the *sodium* salt of *disulphonaphthalene-β-azonaphthalene-α-1-azo-2-hydroxy-3-naphthoic acid*, $C_{10}H_5(SO_3Na)_2 \cdot N{:}N \cdot C_{10}H_6 \cdot N{:}N \cdot C_{10}H_5(OH) \cdot CO_2Na$, which could not be converted into the free acid by boiling with any mineral acid, and forms a black powder. Similarly, *sodium benzidine-bis-1-(azo-2-hydroxy-3-naphthoate)*, $C_{12}H_8[N{:}N \cdot C_{10}H_5(OH) \cdot CO_2Na]_2$, is prepared by coupling a diazotised solution of benzidine with an alkaline solution of 2-hydroxy-3-naphthoic acid. It forms a green powder from which the corresponding free acid is not obtained by means of boiling mineral acids.

The colorations produced when the dyes are dissolved in alkalis or in concentrated sulphuric acid together with the shades produced on unmordanted or chrome-mordanted wool are also described. H. W.

Azo-colouring Matters of Phenyl*iso*ooxazolone. ANDRÉ MEYER (*Compt. rend.*, 1913, **156**, 1992—1995. Compare A., 1911, i, 341).—As the azo-derivatives previously prepared by the author (*loc. cit.*) contained no salt-forming groups and so were unsuited for dyeing purposes, he has now obtained various compounds chemically suitable for dyes, and has compared them with the corresponding pyrazolone compounds.

Sodium phenylisooxazoloneazobenzene-p-sulphonate,

$$C_9H_6O_2N \cdot N_2 \cdot C_6H_4 \cdot SO_3Na, 2H_2O,$$

golden-yellow spangles, obtained by applying a diazotised solution of sulphanilic acid, dyes silk golden-yellow in a bath containing acetic acid.

Sodium phenylisooxazoloneazo-m-xylene-o-sulphonate, an orange, crystalline powder, with $2H_2O$, dyes silk and wool a deep orange-yellow.

Sodium phenylisooxazolone-1-azonaphthalene-4-sulphonate forms orange-brown spangles with $2H_2O$; it dyes silk and wool a reddish-maroon.

Sodium phenylisooxazolone-8-azonaphthalene-2:6-disulphonate, orange crystals with $2H_2O$.

The following substantive dyes were prepared by combining a molecule of a tetrazotised solution of benzidine with a molecule of phenyl*iso*oxazolone, and subsequently coupling the free diazo-radicle with a molecule of a phenol or an amine.

Sodium phenylisooxazoloneazodiphenylazonaphthylaminesulphonate, $C_9H_6O_2N \cdot N_2 \cdot C_6H_4 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(NH_2) \cdot SO_3Na$, obtained by applying naphthionic acid for the second coupling reaction, has a red colour changing to blue on addition of acid; it dyes cotton a scarlet-red.

Sodium phenylisooxazoloneazo-o-ditolylazo-1-amino-8-naphthol-3:6-disulphonate is a reddish-violet powder, changed to bluish-violet by a mineral acid, which dyes a deep violet.

Sodium phenylisooxazoloneazodianisylazo-8-amino-1-naphthol-3:5-disulphonate dyes fabric violet.

Sodium phenylisooxazoloneazodiphenylazosalicylate is a deep brown powder, which dyes cotton orange.

The above dyes are not nearly as fast to light as the pyrazole analogues, the substantive colours being even less stable than the

acid colours mentioned first ; ultraviolet radiation affected the colours much more rapidly than ordinary light. The replacement of the imino-group in such compounds by an oxygen atom evidently provokes a weakening towards photochemical influence according with the lessening in stability towards ordinary chemical agents.   D. F. T.

Existence of Phenyldi-imide. STEFAN GOLDSCHMIDT (*Ber.*, 1913, 46, 2300. Compare this vol., i, 768).—In ethereal solution *p*-bromophenyldi-imide decomposes mainly into *p*-bromobenzene and nitrogen ; quinol and a small amount of a colourless, crystalline substance are also produced in the decomposition.   F. B.

The Density and Volume of Some Protein Solutions. AMEDEO HERLITZKA (*Zeitsch. Chem. Ind. Kolloid*, 1913, 12, 309).— Polemical (compare Chick and Martin, this vol., i, 40 ; Herlitzka, A., 1910, ii, 1013 ; Gayda, A., 1912, i, 399).   J. F. S.

Changes in the Physical Condition of Colloids. XV. Electrochemical Investigations on Acid Protein. KAICHIRO MANABE and JOH. MATULA (*Biochem. Zeitsch.*, 1913, 52, 369—408).— The investigations are a continuation of those of Pauli. The present authors have been chiefly concerned in the determination of the diminution of hydrogen and chlorine ion concentration when hydrochloric acid is added to carefully dialysed solutions of proteins. The hydrogen ion concentrations were determined in the ordinary manner, with the employment of a shaking electrode devised by Pauli, which is figured in the text. The chlorine ion concentration was determined by shaking the solution under investigation with calomel and mercury, and preparing from this mixture a calomel electrode in the ordinary way. The *E.M.F.* was determined when this was balanced against a calomel electrode containing a definite concentration of potassium chloride ($N/10$ or N). A figure is given in which the *E.M.F.* produced is plotted against the hydrogen ion exponent of the mixture under investigation measured against both N and $N/10$-potassium chloride. The form of vessel used for these investigations is also figured in the text. In the cases of albumins, or ox-serum, the addition of acids up to a concentration of $0.03N$ is accompanied by an increased binding of the free hydrogen atoms ; there are, however, only a relatively small number of chlorine ions bound at the same time, and an equality between the hydrogen and chlorine ions bound is only reached in higher concentrations of the acids. If the difference between the bound chlorine and hydrogen ions is plotted against the hydrochloric acid concentration, it will be found that it gradually reaches a maximum and then falls. The maximum corresponds with the maximum of viscosity of the mixture. These results are in accordance with the theory of Pauli, according to whom an albumin hydrochloride is formed, which dissociates in solution giving rise to albumin and chlorine ions ; the high viscosity of the solutions is due to the former. With the addition of increasing amounts of hydrochloric acid, the ionic dissociation of the albumin salt is depressed, and the viscosity

diminishes; an equality between the bound chlorine and hydrogen ions is then also gradually attained. The whole of the hydrogen ions added are never completely bound, and the amount of hydrolytic dissociation of the albumin salt has therefore also been ascertained. For this purpose, the hydrogen ion concentration was determined in an oxserum solution containing $0.02N$-hydrochloric acid in undiluted condition and when diluted with twice and four times its bulk of water. From the numbers obtained, it was calculated that the hydrolytic dissociation amounted to 4.4% in the twice diluted solution, and to 15.3% in the four times diluted solution. The results obtained with gelatin are somewhat different to those obtained with albumins. In this case, there is but little binding of the chlorine ions, even in higher concentrations of acids; the explanation offered in this case is, that the chloride is strongly dissociated even in presence of a large excess of acid. This does not, however, explain the diminution of the viscosity in the higher concentrations; it is suggested that the acid causes, in this case, a degradation of the protein. The effect of the addition of salts to the acid protein solutions was also investigated. This addition causes a small increase in the bound hydrogen ions in low concentrations of acids ($0.005N$-HCl). Such an increase cannot, however, be detected with certainty in the higher concentrations. It is assumed that in this case the salt attaches itself to the acid protein by means of accessory valencies. The actions possible in this case are discussed in some detail. S. B. S.

The Tyrosine Content of Proteins. OTTO FOLIN and WILLEY DENIS (*J. Biol. Chem.*, 1913, 14, 457—458).—Polemical. A reply to Abderhalden and Fuchs (this vol., i, 409). The authors insist that their tyrosine figures are more correct than those hitherto recorded.
W. D. H.

The Factors Concerned in the Solution and Precipitation of Euglobulin. (Miss) HARRIETTE CHICK (*Biochem. J.*, 1913, 7, 318—340).—Re-determination of the isoelectric point of euglobulin shows that it coincides with the point of most rapid agglutination, namely, at a hydrogen ion concentration of about 3×10^{-4} normal. Solution and dispersion of euglobulin by electrolysis is influenced by the nature (especially the valency) of the constituent ions. There are two general types: (1) electrical type of solution in which the dispersion is accompanied by the acquisition of an electric charge by the protein molecules; and (2) molecular type in which the dissolved protein is electrically neutral.

When euglobulin is denaturated by heat, it no longer possesses the property of forming the molecular type of solution. The reaction of acid and alkaline solutions of euglobulin is greatly affected by the addition of electrolytes; the influence of electrolytes in causing precipitation is affected by changes in reaction. Euglobulin in common with caseinogen and vegetable globulins presents an interesting analogy with heat denaturated protein, but differs from it in its capacity to form solutions with electrolytes in which the protein particles are electrically neutral. W. D. H.

Do Gliadin and Zein Yield Lysine on Hydrolysis? Thomas B. Osborne and Charles S. Leavensworth (*J. Biol. Chem.*, 1913, **14**, 481—487).—Small quantities of lysine (as picrate) were separated from the hydrolytic products of gliadin from wheat which had been prepared with great care. Zein yielded none.   W. D. H.

Phonoporphyrin, a New Degradation Product of Hæmin. Oscar Piloty and Hermann Fink (*Ber.*, 1913, **46**, 2020—2026).—In continuation of their work on the molecular size of hæmin and hæmoglobin (A., 1912, i, 923), the authors have further investigated the reduction of hæmin by hydrogen iodide, and have shown that, in addition to mesoporphyrin, a second substance, *phonoporphyrin*, may be isolated, and that the total weight of products thus obtained is 90% of that theoretically derivable from hæmin. Their previous conclusion that the molecular weight of hæmin is 1303 is thus confirmed. The occurrence of phonoporphyrin among the decomposition products of hæmin seems to have been previously observed by Nencki and Zaleski (A., 1901, i, 434), Zaleski (A., 1903, i, 217), and Fischer and Meyer-Betz (this vol., i, 111), but the substance was not further investigated.

When hæmin is boiled with glacial acetic acid, hydriodic acid (D 1·96), red phosphorus and a little water, and the mixture, after removal of phosphorus, poured into a large bulk of water, a mixture of mesoporphyrin and phonoporphyrin is obtained from which the former may be removed by repeated extraction with large quantities of boiling dilute hydrochloric acid. The residual phonoporphyrin, after purification by solution in sodium hydroxide and precipitation with acetic acid, consists of a dark brown, amorphous powder, analyses of which agree most nearly with the formula $C_{34}H_{36}O_7N_4$ or

$$C_{36}H_{40}O_7N_4.$$
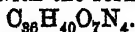
It is not obtained when mesoporphyrin is acted on by hydrogen iodide under the above conditions, and hence cannot be formed as an intermediate product of the formation of mesoporphyrin from hæmin.

When boiled with 9% methyl alcoholic hydrochloric acid, phonoporphyrin yields the corresponding *methyl* ester, $C_{36}H_{40}O_7N_4$ or $C_{38}H_{44}O_7N_4$, which forms minute, brown particles showing no distinct crystalline form, and does not soften at 225°. The similarly prepared *ethyl* ester, $C_{38}H_{44}O_7N_4$ or $C_{40}H_{48}O_7N_4$, decomposes at 255°.

Oxidation of phonoporphyrin in sulphuric acid solution with chromic acid gives methylethylmaleinimide and hæmatic acid, $C_8H_9O_4N$.

H. W.

Histone and its Preparation. Walter H. Eddy (*Biochem. Bull.*, 1913, **2**, 419—440).—Histone, obtained by precipitating aqueous extracts of thymus with ammonia, is different from that obtained by saturation with sodium chloride. The former is not soluble in water, and contains more nitrogen; the latter is soluble in water, and contains combined chlorine.

The preliminary use of alcohol to precipitate histone and the other proteins in the glands is preferable to direct water-extraction. Bang's

contention that ammonia does not precipitate histone in the absence of salts is incorrect; their presence, however, facilitates the process.

W. D. H.

Chondroitin sulphuric Acid. PHŒBUS A. LEVENE and FREDERICK B. LA FORGE (*J. Biol. Chem.*, 1913, **15**, 155—160).—For the first time all the components of this acid were isolated and identified; they are those assumed on indirect evidence by Schmiedeberg, namely, sulphuric acid, acetic acid, glycosamine and glycuronic acid. Schmiedeberg's view of the molecular structure of the molecule needs revision, and the new formula is set out in full. It assumes a glucosidic union of two chondrosin molecules, which explains the reason why chondrosin is a reducing agent, and chondroitin-sulphuric acid is not.

W. D. H.

Sphingomyelin. I. The Presence of Lignoceric Acid among the Hydrolytic Products of Sphingomyelin. PHŒBUS A. LEVENE (*J. Biol. Chem.*, 1913, **15**, 153—154).—Thudichum considered that the principal fatty acid in sphingomyelin was isomeric with stearic acid. This is not so; the acid in question has the composition $C_{24}H_{48}O_2$, melts at 81°, and forms an ethyl ester melting at 55—56°; hence it is lignoceric acid. W. D. H.

The Components of Sphingomyelin. PHŒBUS A. LEVENE (*J. Exper. Med.*, 1913, **18**, 679—680).—By the hydrolysis of this phosphatide the author has obtained in addition to lignoceric acid (preceding abstract) a base, $C_{15}H_{31}O_2N$, which is isolated in the form of its sulphate, m. p. 225°. S. B. S.

Myokynine. DANKWART ACKERMANN (*Zeitsch. Biol.*, 1913, **61**, 373—378. Compare this vol., i, 181).—Myokynine may be prepared from horse as well as from dog muscle. Myokynine dichloride from the dog muscle has $[a]_D^{20} - 11\cdot09°$, that from horse muscle has $[a]_D^{20} - 13\cdot5°$.

Myokynine can be esterified by means of ethyl alcohol and dry hydrogen chloride; it accordingly contains a carboxyl group. It does not give a pyrrole reaction when distilled with zinc dust. Since an unbranched chain of four carbons in presence of basic nitrogen usually forms pyrrole under these conditions, the presence of such a grouping in myokynine is doubtful. E. F. A.

Did Von Wittich Antedate Ostwald in the Definition of Enzyme Action? WILLIAM N. BERG (*Biochem. Bull.*, 1913, **2**, 441—445).—Quotations from von Wittich's writings of 1872-1 show that his conception of enzyme action was much the same as that of Ostwald. He was probably also the first to describe the adsorption of pepsin by solid proteins, such as fibrin. Abderhalden and others who have utilised the method of recent years have not referred to this.

W. D. H.

Amyloclastic Action of Malt and the Reaction of the Medium. HENRI VAN LAER (8th Inter. Cong. App. Chem., 1912, 14, 203—213).—The influence of the addition of varying quantities of acid and alkali on malt extracts of different origin has been studied.

The inhibition resulting from the presence of an excess of acid or alkali is due to the formation of an inactive compound between the enzyme and the acid or alkali. The diminution in the activity of diastase acting in presence of an excess of hydrogen or hydroxyl ions is due to three principal causes: (1) The destruction of a portion of the enzyme—this is non-reversible; (2) the temporary inactivity of part of the enzyme; (3) the increase in the activity due to the disappearance of some of the ions due to the influence of the steadiers (buffers).

Diastase has an amphoteric character, and its specific properties depend on both the acid and basic groups which it contains.

E. F. A.

The Nature of Diastase (Amylase). HENRI VAN LAER (Bull. Acad. Roy. Belg., 1913, 395—451).—A critical examination of previous work on the nature of diastase leads to the conclusion that the enzyme converting soluble starch into maltose is to be regarded as constituted by the association of a colloidal organic nitrogen compound with electrolytes, so allowing the former to act as a catalytic agent, provided always that the reaction of the medium is defined within narrow limits.

Diastase as it exists in cereals differs from the enzyme as used in solution. In the cereal, it is partly present as an insoluble zymogen in combination with protein substances which are capable of attack by pepsin; in solution, the enzyme is free and unaltered either by papain or pepsin.

The organic complement of diastase is digested by a solution of pepsin in hydrochloric acid. It is also modified by phosphotungstic acid like other proteins.

In solutions of diastase the dissolved matter is the more active as the amount of nitrogen in solution increases. The amount of pentosan present bears no relation to the activity of the enzyme. The conclusions are confirmed by extracting powdered diastase with successive equal amounts of water.

In dried preparations the enzyme slowly becomes inactive.

The nitrogen complement of diastase behaves as an amphoteric substance.

The mineral matter is essential for activity, but there is a maximum in the amount of neutral salts, above which any further increase will not cause increased enzyme activity.

At present all the established facts relative to the dynamics of diastatic action are best interpreted on the basis of the properties of emulsoids.

E. F. A.

The Relationship Between the Active and Inactive Condition of a Ferment and its Surface Tension. M. J. GRAMENIZKI (Biochem. Zeitsch., 1913, 52, 142—154).—Taka-diastase

solutions, as the author has already shown, partly recover the activity which has been lost by heating when they are kept. It is now shown that the surface-tensions of the solutions diminish on heating, but again increase on keeping. From these facts, the conclusion is drawn, that there is a connexion between the fermentative activity of a solution and its surface tension. S. B. S.

Saccharification of Starch by Koji Diastase in Presence of Acids and Salts. F. ANDO (*8th Inter. Cong. App. Chem.*, 1912, **14**, 13—24).—Experiments made with an extract of Koji diastase and potato starch in presence of a variety of mineral salts and acids are described. The presence of neutral and acid salts, with the exception of acid calcium phosphate, is up to a certain point favourable to the enzyme. Excess of the salts retards action except in the case of manganese salts.

Alkaline salts, with the exception of potassium phosphate, retard the saccharification. Small quantities of mineral acids accelerate action ; organic acids uniformly retard it. Action takes place in solutions of 30% alcohol. E. F. A.

Some Conditions Affecting the Activity and Stability of Certain Ferments. JOHN H. LONG and WILLIAM A. JOHNSON (*J. Amer. Chem. Soc.*, 1913, **35**, 895—913).—It is suggested that for diastasic comparisons, the starch paste should be made from starch prepared in the laboratory from sound ripe potatoes, and subsequently well washed. In experiments in which 0·1 gram of sodium chloride was present in each 100 c.c. of digesting mixture, it was found that amylolytic activity is greatest when about 25 mg. of sodium hydrogen carbonate are also added ; sodium hydrogen carbonate in larger quantity retards the action without destroying any of the ferment, whilst the addition of sufficient acid to neutralise the hydrogen carbonate destroys the ferment at once. Glycerol extracts of the pancreas are very stable, but rapidly lose amylotic power after dilution, especially if kept at 40° ; the presence of traces of sodium chloride exerts a considerable protecting effect. Experiments with the glycerol extract indicate that the pancreatic diastase is exceedingly sensitive towards even traces of mineral acid, such as hydrochloric acid, but that salt again exerts a protecting action ; the effect of the acid, which is more marked than that of alkali, is probably due to immediate destruction of the enzyme, as neutralisation fails to restore the original activity. D. F. T.

The Nature of Enzyme Action. III. The Synthetic Action of Enzymes. WILLIAM M. BAYLISS (*J. Physiol.*, 1913, **46**, 236—266).— Reactions in the system glycerol, dextrose, glycerol-glucoside and water, as accelerated by emulsin, follow the laws deduced from mass action for an equilibrium in a reversible system, catalysed by a single enzyme. The equilibrium position is the same from whichever end it is approached ; the glucoside produced is the β-form, and the same which is hydrolysed by emulsin. The reaction-rate is directly proportional (not linear, how-

ever) to the concentration of the enzyme. The final equilibrium is independent of this concentration.

Brailsford Robertson's "synthesis of paranuclein by pepsin" is not a synthesis, nor is it produced by pepsin; the substance formed is not paranuclein. It is a colloidal precipitation, and has no connexion with enzyme action.

Apparent deviations from the law illustrated should be properly investigated, and the reasons for divergence sought. It is unwise to invent new enzymes to explain difficulties.   W. D. H.

The Lipases Contained in Pancreatic Cysts. KONRAD BOURNOT (*Biochem. Zeitsch.*, 1913, 52, 155—171).—The lipases from the fluids of pancreatic cysts are similar to other animal lipases. The liquids can be filtered through paper without loss of lipolytic activity. This continually diminishes if the liquid is kept, but the residue obtained by evaporation at 20° preserves its lipolytic activity. Acids inhibit the lipolytic action, but alkalis in very low concentrations accelerate it. With small quantities of fluids (0·05—0·2 c.c.) there is a direct proportionality between the amount of enzyme and the fat saponified. For larger quantities of ferment the formulæ of Schütz and Arrhenius hold good. The Schütz law and Arrhenius' equation also agree with the time relations in fat hydrolysis and the oleic acid-glycerol fat synthesis within certain limits. Still better agreement is obtained, however, with the employment of contents calculated from the adsorption isotherm $K = X/E^m$. The maximal hydrolysis of triolein obtained was 93·5%, and the maximal synthesis in the presence of excess of glycerol was 42% of the oleic acid.   S. B. S.

The Lipase of Chelidonium Seeds. KONRAD BOURNOT (*Biochem. Zeitsch.*, 1913, 52, 172—205).—Like the ricinus lipase, the chelidonium lipase is insoluble in water, but is, to a large extent, soluble in the oils extracted by ether from the seeds. It is also somewhat soluble in a mixture of oleic acid and alcohol. Whereas, however, the ricinus lipase acts most readily on addition of acids, the chelidonium ferment acts best in the presence of water alone. Even $N/50$-acetic acid has an inhibitory effect on its action. The maximal hydrolysis obtained was 92—95%. The lipases of ricinus and chelidonium are similar, in ·that they do not readily hydrolyse the esters of the monohydroxy-alcohols. As the molecular weights of the fatty acids increase, the esters are more rapidly attacked by the chelidonium lipase; thus, *iso*butyl oleate and amyl palmitate undergo hydrolysis to the extent of 15—33%. The lipase, furthermore, can cause a rapid and almost complete synthesis of the esters of the higher fatty acids, which action is in marked contrast to the less complete hydrolysis of the same esters caused by the ferment. Possibly the larger quantities of water have an inhibitory action when the water of the substrate cannot form an emulsion. The *iso*butyl oleate synthesis accords with a unimolecular reaction, and there is a direct proportionality between the rate and quantity of enzyme present. The maximal synthesis is 92%. The maximal triolein synthesis is 47—50%. In the latter cases, the same final equilibrium is obtained in synthesis and hydrolysis. The final equilibrium here will depend

on the amount of water present. The seeds can be heated for fifteen minutes at 100° without any very marked deterioration of the ferment.　　　　　　　　　　　　　　　　　　　　　　　　S. B. S.

Action of Boric Acid on Zymase; Comparison with the Action of Phosphates. HENRI AGULHON (*Compt. rend.*, 1913, 156, 1855—1858).—The author has previously shown (A., 1909, i, 621) that boric acid is remarkably inactive towards diastases in general, and has examined its action on zymase. For this purpose, sucrose or dextrose was mixed with a constant quantity of zymase in the presence of varying amounts of boric acid, the course of the reaction being followed by determining from time to time the loss in weight due to the carbon dioxide evolved. The inhibiting action of boric acid is observable even with only 10 mg. of acid per 100 c.c., whilst with one gram of acid per 100 c.c. fermentation is no longer possible. On the other hand, living yeast derived from the same source is capable of fermenting a portion of the sugar supplied to it even in the presence of boric acid of the concentration 2 in 100, from which it appears that the membrane presents contact of the boric acid with the zymase.

The inhibiting action of boric acid cannot be attributed solely to its acidity, since monosodium phosphate, which possesses the same degree of acidity as boric acid, exerts a slight favouring action. The nature of the electronegative radicle is also important. This is shown by a series of comparative experiments with borax, trisodium phosphate, trisodium citrate, and sodium carbonate, in which only the borax is found to have a marked inhibiting effect. This effect is, however, less than that observed with boric acid, so that it appears that the favouring action of the alkali compensates in some measure the inhibiting action of the electronegative radicle.　　　　　　　　　　　　　　　　H. W.

Physiological Chemistry

The Work Done by the Lungs at Low Oxygen Pressures. ARCHIBALD V. HILL (*Proc. physiol. Soc.*, 1913, xxvii—xxviii; *J. Physiol.*, 46).—By calculation, from known data, of the work done by the lungs in secreting oxygen (if Haldane's views are accepted) it is found that the work done per minute by the lungs is only 0·8 cal. If therefore the lung cells can secrete oxygen at all, and if they be assumed to possess an "efficiency" in performing the mechanical work of oxygen secretion of only 20%, they should, nevertheless, be well able to perform this work with an activity no greater per gram than that of the body as a whole.　　W. D. H.

Carbon Dioxide Excretion Resulting from Muscular Work following Forced Breathing. GEORGE O. HIGLEY (*Biochem. Bull.*, 1913, 2, 390—392).—The sudden increase in the excretion of

carbon dioxide after the beginning of work is due to better ventilation of the lungs; the continuation of the increase is due to ventilation of the blood and tissues also. After forced breathing, followed by muscular work, the new rate of excretion is sharply defined; the further increase as the result of work is not so prompt, and comes on gradually. Some differences of detail occur according to the duration of the forced breathing.   W. D. H.

The Influence of Barometric Pressure on the Excretion of Carbon Dioxide in Man. G. O. HIGLEY (*Biochem. Bull.*, 1913, **2**, 393—402).—The degree of influence of barometric pressure on the excretion of carbon dioxide differs in different subjects. It is evidently a minor factor, the effect of which is liable to be masked by other influences, diet, exercise, etc.   W. D. H.

The Effect of Altitude on Mesectic Curves. JOSEPH BARCROFT (*Proc. physiol. Soc.*, 1913, xxx—xxxi ; *J. Physiol.*, **46**).—In subjects at rest living at a high altitude there is a reduced carbon dioxide tension in the blood, and acidosis. These so nearly balance each other that the dissociation curve remains mesectic (that is, normal). This statement is illustrated by the necessary data and calculations.
     W. D. H.

The Relation of the Blood-salts to Cardiac Contraction. ERNEST G. MARTIN (*Amer. J. Physiol.*, 1913, **32**, 165—183).—Calcium and sodium are not regarded as antagonistic, but each has a definite function. Calcium promotes (as Howell stated) the conversion of stable into unstable energy-yielding material; sodium (as proposed by Lingle) serves as the immediate stimulus to bring about the actual dissociation, and so to initiate the heart-beat. Neither is an exclusive agent; the preparation of dissociable material is much hampered by the accumulation of waste products, and is therefore aided by abundant supplies of oxygen or by sodium carbonate; carbon dioxide in moderate quantities, and perhaps sugar, act as direct stimulants to cardiac tissue much as sodium acts.
     W. D. H.

Hæmolysis by Silicic Acid. M. LIEBERS (*Arch. Hygiene*, 1913, **80**, 43—55).—In the system blood + silicic acid + complement, hæmolysis often takes place. The silicic acid cannot, however, always replace an ordinary amboceptor. Certain complements show the same complementing action towards sheep corpuscles charged with silica as towards the same corpuscles charged with an ordinary amboceptor. The more coarsely colloidal or turbid solutions of silica cause agglutination, and the blood does not then lake so readily when treated with the complement. The ordinary immune amboceptor in the original Wassermann reaction cannot be replaced by silica.   S. B. S.

Lipolytic Action of the Blood. FRANCIS H. THIELE (*Biochem. J.*, 1913. **7**, 275—286).—Blood and chyle contain an enzyme which can hydrolyse lecithin, but not neutral fat. When blood and chyle fat

are incubated together, the neutral fat forms an absorption compound with the protein, and is then non-extractable by ether. This compound can be broken up by peptic digestion, by alcohol, and by heating. The formation of the complex occurs in the corpuscles; serum has no such effect. It is not due to hæmoglobin, and is probably brought about by an enzyme.   W. D. H.

Variations in Glycæmia during Inanition. HENRY BIERRY and (Mlle.) LUCIE FANDARD (*Compt. rend.*, 1913, **156**, 2010—2013).— The authors have already shown (this vol., i, 426) that the injection of adrenaline can induce perturbations in the glycæmia of an animal, and now bring evidence of the considerable effect on the content of sugar in the blood of dogs caused by inanition. The quantity of free sugar is fairly constant for the first twelve days, then may occasionally increase considerably, but finally decreases. The combined sugar, which is liberated on hydrolysis, commences to increase in quantity about the twelfth day and continues to increase until death.   D. F. T.

The Action of the Thromboplastic Substance in the Clotting of Blood. F. W. MACRAE and A. G. SCHNACK (*Amer. J. Physiol.*, 1913, **32**, 211—218).—Calcium-free (oxalated) peptone plasma may be made to clot by the addition of calcium-free solutions of thromboplastic substance (kephalin), provided the excess of oxalate is removed by dialysis. The action of the kephalin is demonstrated more easily if some thrombin is added previously to the dialysed oxalate plasma in an amount insufficient in itself to overcome the effect of antithrombin. This result is opposed to the theory of Morawitz that the thromboplastic substance acts as a kinase in conjunction with calcium, but accords with Howell's view that kephalin facilitates clotting by neutralising antithrombin.
    W. D. H.

Blood-relationship of Animals as Displayed in the Composition of the Serum-proteins. II. A Comparison of the Sera of Ox, Sheep, Hog, Goat, Dog, Cat, and Guinea-pig with Respect to their Content of Various Proteins. J. HOMER WOOLSEY (*J. Biol. Chem.*, 1913, **14**, 433—439).—The following table summarises the average results obtained:

	Percentage of the total proteins in the sera of						
	Ox.	Sheep.	Hog.	Goat.	Dog.	Cat.	Guinea-pig.
"Insoluble" globulin...	8·1	6·4	6·0	6·5	7·7	6·5	4·2
Total globulin	29·0	17·0	36·0	22·0	18·0	30·0	16·0
Total albumin	70·0	82·0	64·0	75·0	81·0	69·0	84·0

    W. D. H.

The Activation of Blood-serum. CORNELIS A. PEKELHARING (*Zeitsch. physiol. Chem.*, 1913, **85**, 341—345).—When blood-serum is kept, its power to coagulate fibrinogen lessens. Morawitz attributes this to a change of thrombin into a metathrombin. Such serum

can be reactivated by adding alkali, and then neutralising; the author advances the view that the loss of activity is due to the development of inhibitory substances, and that these are destroyed by alkali. He also disagrees with Landsberg, who regards the loss of activity as due to adsorption of the thrombin by the serum proteins; and quote experiments to support his view. Among other things proved is the fact that dialysis of the serum removes the inhibitory substance or substances. Activated serum on keeping loses its activity more rapidly than serum which has not been treated with alkali.   W. D. H.

The Digestive Enzymes of Cold- and Warm-blooded Animals. I. The Pepsin of the Hake and Dog. A. RAKOCZY (*Zeitsch. physiol. Chem.*, 1913, **85**, 349—371).—The pepsin of hake and dog are not identical, but show the following differences: Hake pepsin digests fibrin, serum protein, and caseinogen well, but it is less active towards edestin, and especially towards egg-albumin and elastin than dog's pepsin. Hake pepsin is adapted to work at a lower acidity than dog's pepsin; there are also differences in milk-curdling power, adsorption by elastin, velocity of action, and in optimum temperature. Hake's pepsin is only slightly inhibited at freezing point.   W. D. H.

The Pepsin–Chymosin Question. WILLEM VAN DAM (*Zeitsch. physiol. Chem*, 1913, **86**, 77—84).—Polemical against Rakoczy's views.   W. D. H.

The Influence of Preliminary Heating on Peptic and Tryptic Digestion. A. H. BIZZARRO (*J. Physiol.*, 1913, **46**, 267—284).— During peptic digestion, Sörensen's formaldehyde method shows that amino-acid groupings are liberated slowly, and after many days' action the time varies for different proteins. Preliminary heating of egg-white to 120—140° makes subsequent tryptic proteolysis more active; the same is true for fibrin, caseinogen, and beef; but the opposite for gelatin. The amino-acid groupings in tryptic solutions increase after fifteen hours' digestion.   W. D. H.

Pancreatic Digestion. (Miss) GERTRUDE D. BOSTOCK (*Zeitsch. physiol. Chem.*, 1913, **85**, 471—492).—A study of the influence of alkali on the partition of nitrogen in the digestion of fibrin by pancreatin shows that the powers to dissolve and to split proteins are two different things. The most favourable degree of alkalinity for protein solution is between 1·2 and 1·8% of sodium carbonate. Protein cleavage is hindered by 0·6% sodium carbonate, but between 0% and 0·3% no differences were noted. An optimum concentration for cleavage was not found. The cleavage during protein tryptic digestion is as unfavourably influenced by 0·6 to 1·2% of sodium carbonate as is protein cleavage during autolysis.
                                    W. D. H.

The Influence of Carbon Dioxide on Chlorine Metabolism. ERNST LAQUEUR and J. SNAPPER (*Biochm. Zeitsch*, 1913, **52**, 41—59). —It has been shown by Hamburger that chlorine passes from the

body fluids into tissue cells when the mixture is treated with carbon dioxide *in vitro*. Experiments carried out with rabbits, which were allowed to inhale air rich in carbon dioxide, failed to reveal a similar action *in vivo*, as no chlorine retention was found to take place after such inhalations, as should be expected if chlorine passed from the blood serum into the formed elements. It is assumed that the body possesses some compensatory mechanism which prevents this from taking place. S. B. S.

The Nitrogen-sparing Action of Salts, Especially of Sodium Acetate, in the Case of Carnivorous Animals. ERNST PESCHECK (*Biochem. Zeitsch.*, 1913, **52**, 275—330).—Numerous experiments are given in detail, in which sodium acetate and other salts were added to basal diets given to dogs, in which the nitrogen balance was, in some cases, complete, in other cases positive, and in still other cases negative. The results of previous experiments were confirmed, which tended to show that sodium acetate causes nitrogen retention, this action being specially marked when the nitrogen balance is a negative one. The salt is without action on the amount of nitrogen excreted in the fœces. Sodium citrate, sodium lactate, and magnesium acetate appear to exert a similar action. The author supposes that the action is due to the alkali added, which can be used for neutralisation of acids in the body, instead of the ammonia set free by the deamidisation of the proteins. S. B. S.

[Nitrogenous Metabolism.] EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, **85**, 347—348).—Polemical. A final reply to Abderhalden and Lampé (compare this vol., i, 547, 671). W. D. H.

The Normal Protein Metabolism of the Rat. OTTO FOLIN and J. LUCIEN MORRIS (*J. Biol. Chem.*, 1913, **14**, 509—515).—The new micro-chemical analytical methods enable small quantities of urine to be dealt with, such as are excreted by the rat. Rat's urine closely resembles that of man. The high percentage of uric acid is remarkable, for the rat's tissues lack the uric acid-forming enzymes, although the liver destroys it. W. D. H.

Intermediary Metabolism of Carbohydrates and Proteins. The Mutual Interconversion of α-Amino-acids, α-Hydroxy-acids, and α-Ketonic Aldehydes. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, **14**, 555—561; **15**, 127—143).—By a suitable choice of experimental conditions it is possible to convert α-amino- and α-hydroxy-acids into α-ketonic aldehydes at low temperatures; lactic acid and alanine. for example, yield methylglyoxal. When methylglyoxal is acted on by enzymes (glyoxalases) found in the body, *d*- and *l*-lactic acid are formed. When given to the glycosuric animal, glyoxal and both lactic acids yield dextrose. Methylglyoxal is therefore believed to be an intermediate product in the mutual interconversion of alanine, lactic acid, and dextrose (compare Proc., 1913, **29**, 156). W. D. H.

The Value of Lactose and Galactose after Partial Exclusion of the Liver (Eck's Fistula). LUDWIG DRAUDT (*Arch. expt. Path. Pharm.*, 1913, 72, 457—474).—After an Eck's fistula the nutritive value of lactose and galactose falls; the liver fails to convert them into glycogen, and the sugars circulate in the blood and leave the body by the urine. 　　　　　　　　　　　W. D. H.

The Formation of Fat from Carbohydrate. SERGIUS MORGULIS and JOSEPH H. PRATT (*Amer. J. Physiol.*, 1913, 32, 200—210).—The present observations on dogs confirm the results of others with other animals, that feeding on carbohydrates leads to fat formation with the accompaniment of a high respiratory quotient. 　　　　　　　　　　　W. D. H.

Fat Absorption. II. Absorption of Fat-like Substances other than Fats. W. R. BLOOR (*J. Biol. Chem.*, 1913, 15, 105—117).—Neither petroleum hydrocarbons nor unsaponifiable esters (wool-fat) are absorbed. Neither class of compounds is reducible to a water-soluble form in the intestine. Hence it is extremely probable that fats can only be absorbed in water-soluble form, and that saponification is a necessary preliminary to absorption. 　　　　　　　　　　　W. D. H.

The Absorption of Nitrogenous Products. OTTO FOLIN and WILLEY DENIS (*J. Biol. Chem.*, 1913, 14, 453—455).—Polemical. A reply to Abderhalden and Lampé (A., 1912, ii, 1189). W. D. H.

Nutrition of the Embryo-chick III. The Assimilation of Egg-white. HUBERT W. BYWATERS and W. BARRETT ROWE (*Proc. physiol. Soc.*, 1913, xxxiii—xxxiv; *J. Physiol.*, 46).—During incubation the ratio of albumin to ovomucoid in the white of the egg remains constant. Either the two proteins are absorbed at the same rate or the albumin alone is absorbed, and then fresh albumin is formed from the ovomucoid. The ovomucoid contains the same proportion of carbohydrate throughout. Probably the first explanation is the correct one. 　　　　　　　　　　　W. D. H.

An Important Chemical Difference between the Eggs of the Sea Urchin and those of the Star-fish. ALBERT P. MATHEWS (*J. Biol. Chem.*, 1913, 14, 465—467).—Cholesterol is absent or nearly so in the starfish egg. It could not be found in the eggs of *Asterias forbesii*. It is present in considerable amount in the sea urchin eggs. The phosphatide of the starfish contains about 10% of a reducing sugar in firm combination and also sulphuric acid. 　　　　　　　　　　　W. D. H.

The Influence of Hypertonic Solution on the Rate of Oxidations in Fertilised and Unfertilised Eggs. JACQUES LOEB and HARDOLPH WASTENEYS (*J. Biol. Chem.*, 1913, 14, 469—480).—The unfertilised eggs of sea urchins which have undergone artificial membrane formation die if not treated with a hypertonic solution,

but the solution does not increase the rate of oxidations either in unfertilised or fertilised eggs. Such solutions increase the rate of oxidations in unfertilised eggs if they have not undergone membrane formation. Weak bases added to normal sea-water cause membrane development, and affects the rate of oxidation in unfertilised eggs as when they are added to hypertonic sea-water. Complete cytolysis of the unfertilised eggs by saponin raises the rate of oxidation to the same height as fertilisation, showing that cytolysis of the surface of the egg is the essential feature in fertilisation.

W. D. H.

The Influence of Bases on the Rate of Oxidations in Fertilised Eggs. JACQUES LOEB and HARDOLPH WASTENFYS (*J. Biol. Chem.*, 1913. **14**, 459—464).—Bases influence the rate of oxidations differently in the fertilised and unfertilised eggs of *Strongylocentrotus purpuratus*. Strong bases accelerate this rate in the fertilised egg only if their concentration is over $10^{-3}N$; this suppresses development of the egg. Weak bases accelerate the rate slightly in the fertilised egg. No conclusion as to the seat of oxidation in the egg is warranted.

W. D. H.

Biochemistry of Protozoa. II. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **86**, 33—42).—The parasitic protozoon *Goussia gadi*, which lives in the swim-bladder of certain fishes and also in shellfish, was investigated.

The composition and constants of the fatty substances present show them to be different from those in the host. No sugar or related substance was found. The keratin-like protein in the spore-capsules is free from sulphur and phosphorus. After hydrolysis, lysine, histidine, arginine, tyrosine, glycine, and glutamic acid were separated.

W. D. H.

The Action of Tissues on Hexoses. PHŒBUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem.*, 1913, **15**, 65—68).—Kidney tissue was obtained aseptically, and in its presence dextrose, *d*-mannose, and *d*-fructose were all converted into *d*-lactic acid. The action is the same, but not quite so powerful as that of leucocytes.

W. D. H.

The Biochemical Conversion of Methylglyoxal into Lactic Acid and the Formation of the Different Lactic Acids in Nature. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **51**, 484—508).—Animal tissue extracts contain an aldehydomutase, which readily converts methylglyoxal into lactic acid. The reaction takes place best when the reaction mixture contains calcium hydrogen carbonate, which prevents the mixture from becoming too acid. This process is carried out in the following way: 1·40 grams of calcium carbonate are added for each 0·72 gram of methylglyoxal present in solution in the organ extract; the former is added, and the liquid is saturated with carbon dioxide before addition of the aldehyde. After remaining in the incubator, the mixture is heated

and filtered, and an aliquot portion is evaporated to a small bulk. Hot alcohol is added, the precipitated substances were filtered off, the filtrate is again evaporated, treated with alcohol, and again evaporated. These processes are continually repeated until no precipitate is produced on addition of alcohol. The amount of lactic acid formed can be estimated by determining the amount of calcium in an aliquot part of the final filtrate; for determination of the rotation the zinc salt can be made from this liquid. Control estimations should be made with the methylglyoxal and tissue extract separately, both of which yield small quantities of a soluble calcium salt when treated by the above process, and a correction can be thus introduced into the result.

The conversion of methylglyoxal into lactic acid is never quantitative, but reaches sometimes 75%. Certain maceration juices of top yeasts are also capable of producing lactic acid from methylglyoxal, but not aqueous extracts of the same. The lactic acid thus produced is inactive. On the other hand, muscle and liver extracts produce the l-acid, which is not the naturally occurring form. The theory of the formation of this active form is discussed by the author in some detail. He assumes that by the addition and scission of the elements of water optically active substances can be produced from forms such as methylglyoxal, which are themselves inactive, and that such active substances are formed as intermediary products in various biochemical changes. These views are illustrated by numerous examples and formulæ.   S. B. S.

The Preparation from Animal Tissues of a Substance which Cures Polyneuritis in Birds Induced by Diets of Polished Rice. I. EVELYN A. COOPER (*Biochem. J.*, 1913, 7, 268—274).— A fraction rich in the anti-neuritic substance can be precipitated by ether from the fats and lipoids (alcoholic extract) of horse-flesh. The substance is insoluble in alcohol, benzene, chloroform, ether, and ethyl acetate, but is moderately soluble in water. It is absorbed to some extent by animal charcoal, and is destroyed readily by alkali. Quinine and cinchonine exert a temporary curative action in these birds, but lose this power after being heated at 125° for six hours; the effect is regarded as due to traces of the anti-neuritic substance from the cinchona bark. Alcohol given to the birds in small doses does not affect the onset of polyneuritis when a diet of polished rice is taken. This suggests that alcoholic neuritis is not due to a lessened capacity of the body to utilise the anti-neuritic substance.   W. D. H.

Lipolytic Action of the Tissues. FRANCIS H. THIELE (*Biochem. J.*, 1913, 7, 287—296).—The tissues possess a true lipolytic enzyme, but, except in the case of the pancreas, it hydrolyses phosphatides and jecorins, but not ordinary fats. It acts in an alkaline or acid medium. There is no evidence of a kinase in the spleen.
        W. D. H.

The Influence of Anæsthetics on the Oxydones. FRÉD. BATELLI and (Mlle) LINA STERN (*Biochem. Zeitsch* 1913. **52**, 226—252. Compare Vernon, this vol., i, 220).—The "oxydones" are the insoluble catalysts contained in animal tissues, which accelerate the oxidation of certain substances. Below certain concentrations, anæsthetics have no action on the succinic oxydone; at a certain critical concentration they exert an inhibitory influence, which is not far removed, except in the case of antipyrine, from a limiting concentration at which the ferment becomes quite inactive. Similar phenomena were observed by Vernon in the case of the phenylenediamine oxydone. All anæsthetics have the power of precipitating nucleoproteids from aqueous solution; this precipitation is only marked when a certain critical concentration is reached, and is complete in a slightly higher concentration. These two concentrations, except in the cases of phenol and *o*-cresol, are almost identical with the concentrations necessary for inhibition and complete inactivation of the oxydone. They also vary, in both cases, with the temperature. The influence of the anæsthetics on the activity of the succinic oxydone is not much stronger when they are present during the actual oxidation than when the tissue has been treated by them and then washed. The destruction of the oxydone is therefore an irreversible process. There is, as Vernon has already shown, a parallelism between narcotic action and capacity to destroy oxydones, which is far more marked than the parallelism between the narcotic action and coefficient of distribution between oil and water. There is also a parallelism between the capacity for destroying oxydones and the hæmolytic action, the toxicity, and capillary activity. The authors draw the conclusion that these activities are due rather to actions on the proteins than to the actions on lipoids   S. B. S.

The Influence of Aldehydes on the Oxydones FRÉD. BATELLI and (Mlle) LINA STERN (*Biochem. Zeitsch* , 1913. **52** 253—270).—The aldehydes are similar in their action on oxydones to the anæsthetics, the method of action of which is described in the preceding paper. There is a critical concentration at which inhibition is effected, which is not far removed from the limiting concentration of total inactivation. Both vary with the temperature; the destructive action on the oxydones, furthermore, is an irreversible one. These critical and limiting concentrations do not coincide, however, with the incipient and complete precipitation of the nucleoproteins in the case of liver extracts, but, as a general rule, they nearly coincide with the capacity of the aldehyde to form a precipitate with the soluble proteins after acidification with acetic acid. Again, the authors draw the conclusion that the destruction of oxydones is due rather to action on the proteins than to action on the lipoids.   S. B. S.

The Sympathetic System Does Not Possess the Same Chemical Composition as the Axial Nervous Tissue and the Cranial or Spinal Nerves. N ALBERTO BARBIERI (*Compt. rend.*, 1913, **157**, 69—72).—By successive extraction with carbon

disulphide, distilled water, alcohol, ether, and boiling alcohol the author has made a comparative analysis of the tissue of the sympathetic system and of the axial nervous tissue and the cranial and spinal nerves, and finds that the first-named differs in chemical composition from the others. Of its total extract 66% is composed of oil and stearin. It is completely void of nervous serum and of cerebroin and cerebrin.   W. G.

Carbon Dioxide Production in Nerve Fibres. SHIRO TASHIRO (*Amer. J. Physiol.*, 1913, **32**, 107—136).—All nerve fibres give off carbon dioxide. A nerve of the spider crab at rest produces $6\cdot7 \times 10^{-7}$ gram per 10 mg. per ten minutes. The figure for frog's sciatic is $5\cdot5 \times 10^{-7}$. The amount is increased in activity to 16×10^{-7} (crab) and $14\cdot2 \times 10^{-7}$ (frog). This is due to a vital active process, which is reduced by anæsthetics, both in nerves and seeds.   W. D. H.

The Cerebro-spinal Fluid in Nervous Diseases. I. ROBERT V. STANFORD (*Zeitsch. physiol. Chem*, 1913, **86**, 43—50).—The high specific gravity of the cerebro-spinal fluid in cases of progressive paralysis is regarded as of diagnostic importance.   W. D. H.

The Cerebro-spinal Fluid in Nervous Diseases. II. Nitrogen. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, **86**, 219—233) — The amount of nitrogen follows the specific gravity; it is increased in progressive paralysis, and in certain other mental diseases, but not so greatly. In epilepsy this is not the case as a rule.
                                                        W. D. H.

The Action of Electrolytes on the Heart. GEORGE R. MINES (*J. Physiol.*, 1913, **46**, 188—235).—The experiments were made on the frog's heart, simultaneous records of the contractions and of their electrical accompaniment being taken. The character of the electrocardiogram and the changes it undergoes are discussed at length. Among the points of interest noted is that the electrical changes may continue after all movements have ceased, as when calcium is absent from the perfusing fluid. This has already been noticed in the mammal's heart by Locke and Rosenheim.
                                                        W. D. H.

The Action of Pituitrin and β-Amino-4 ethylglyoxaline (Histamine) on the Action of the Heart. W. EINIS (*Biochem Zeitsch.*, 1913, **52**, 96—117).—The experiments were made on the isolated hearts of frogs and rabbits. In the rabbit's heart single small doses of pituitrin cause a slight increase in the frequency, larger doses a diminution. Repeated doses also cause a diminution In hearts brought to a standstill by want of oxygen, pituitrin causes a transient activity. β-Amino-4-ethylglyoxaline causes a diminution of frequency by inhibition of the stimulus. On the mammalian heart pituitrin causes a diminution of frequency, followed by a more or less marked rise; there is a diminution in

the height of contraction, followed by a recovery to the normal, or even higher than the normal. The diminution in the frequency and height of contraction may be ascribed to the chloretone contained in the preparation used. β-Amino-4-ethylglyoxaline causes an increase in the frequency in the mammalian heart to two or three times the normal after a slight preliminary transient diminution. The final value is below normal. It also causes a marked increase in the height of contraction.   S. B. S.

The Action of the Diastatic Ferment on Glycogen within the Cell. III. ERNST J. LESSER (*Biochem. Zeitsch.*, 1913, 52, 471—485).—During the winter months glycogen does not disappear quickly from the liver during incubation of the intact organ. If, however, the organs are ground up so as to destroy the structure, the glycogen rapidly disappears; in fact, it is hydrolysed as rapidly as it is in the intact organs taken from animals during the months of May and June, when the glycogen is labile. The difference is probably due to the difference of the diffusibility of the ferment through the cells, which enables it to come into contact with the glycogen, and not to the presence of blood-diastase, as the same results are obtained with the organs which have been perfused and rendered blood-free, as with the organs directly removed from the body (compare Ivar Bang, this vol., i, 552, 553).   S. B. S.

The Action of Antiglycosuric Medicaments and Liver Glycosuria. III. The Perfusion of the Liver with Blood under the Influence of Different Reagents. ERNST NEUBAUER (*Biochem. Zeitsch*, 1913, 52, 118—141. Compare A., 1912, ii, 962).—The results were obtained by oncometric experiments on rabbits' livers. An increase of volume of the organ follows the intravenous or subcutaneous injection of adrenaline, and the intravenous injection of the infundibular portion of pituitary body, of strophanthin, of cocaine (after subcutaneous injection of adrenaline), after asphyxia produced by stoppage of the trachea, after faradic stimulation of the central end of the vagus in the neck and the stimulation of the splanchnic. There is contraction or inhibition of expansion of the liver, after intravenous injection of the glandular portion of the pituitary body, after veronal, chloral hydrate, ergotoxin, after venesection, and after stimulation of various kinds of the peripheral end of the vagus. Phloridzin and cocaine have no specific action on the liver volume. Caffeine and diuretin cause repeated alterations in the kidney volume. The liver volume changes run as a rule parallel with the height of the blood-pressure, behaving in this respect like the limbs, but unlike the spleen. Those treatments of the animals which produce hyperglycæmia in the liver through vaso-constriction in the splanchnic vessel system cause, generally, expulsion of the sugar, whereas those treatments which antagonise this stasis in the liver, antagonise also glycosuria. The rule is, however, not absolute; diminution of the liver volume produced by insufficient arterial blood supply, for example, can also be accompanied by expulsion of sugar, which also takes place in a stasis produced by anoxybiotic conditions.   S. B. S.

The Oxidation Products of Cholesterol in the Animal Organism (Portal and Hepatic Veins). V. ISAAC LIFSCHUIZ (*Biochem. Zeitsch.*, 1913, **52**, 206—213).—The absence of oxycholesterol from the liver might be explained, either on the assumption that the liver cannot take up this substance, or that it takes it up from the blood-stream and changes it into other products which do not give the oxycholesterol reactions. From analyses of the blood of the portal and hepatic veins, and of blood which had been artificially perfused through the liver, the second of the above explanations seems to be correct, for the hepatic vein contains less oxycholesterol than the portal vein, and unperfused blood less than perfused blood.   S. B. S.

The Effect of Changes in the Circulation of the Liver on Nitrogen Metabolism. SAMUEL A. MATTHEWS and E. M. MILLER (*J. Biol. Chem.*, 1913, **15**, 87—104)—After an Eck fistula is established, urea in the urine is largely replaced by ammonia, and toxic effects have been described as the result of increased ammonia in the blood. In the present experiments a large number of the dogs died of inanition, but in some the augmented excretion of ammonia over long intervals did not even produce ill health. Such dogs, however, are susceptible to meat intoxication. In animals which survive a long time the formation of adhesions may bring about a partial return of portal blood to the liver.   W. D. H.

Physiology and Pathology of the Kidney Functions. WILHELM BAETZNER (*Archiv expt. Path. Pharm.*, 1913, **72**, 309—315).—In experiments on animals it was found contrary to the statements of Bock that in water diuresis a regularly increasing rise in phosphorus elimination takes place.   W. D. H.

Action of Leucocytes on Hexoses. IV. The Mechanism of Lactic Acid Formation. PHŒBUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem.*, 1913, **14**, 551—554).—The present paper confirms the work of Dakin and Dudley (this vol., i, 565; also corroborated by Neuberg, this vol., ii, 564) on the existence of glyoxalases. In the present experiments bacteria were rigidly excluded. Leucocytes and kidney tissues were used, and produced the conversion of methylglyoxal into *dl*- and *d*-lactic acid. This confirms the view that the formation of *d*-lactic acid from the various *d*-hexoses is conditioned by the intermediate formation of methylglyoxal:

$$OH \cdot CH_2 \cdot CH(OH) \cdot CHO \longrightarrow CH_3 \cdot CO \cdot CHO \longrightarrow$$
$$CH_3 \cdot CH(OH) \cdot CO_2H.$$

W. D. H.
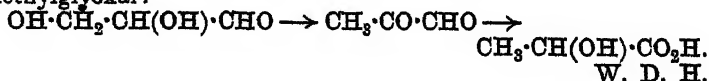
The Physiology of the Thyroid. F. BLUM (*Zeitsch. physiol. Chem*. 1913, **85**, 428—429).—Introductory to a series of papers to follow later.   W. D. H.

Self-digestion of the Thymus. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, **15**, 81—84).—In self-digestion of the thymus, the

enzymes present are not capable of decomposing all the nucleic acid within any reasonable length of time; the portion left undecomposed appears to be identical with that prepared from the fresh gland. W. D. H.

Physical Chemistry of Muscle-plasma. FILIPPO BOTTAZZI (*Biochem. Bull*, 1913, **2**, 379—385).—Muscle-plasma as seen under the ultra-microscope is full of many brilliant, small particles (myosin) and a small number of coarse particles; the latter are composed of fat, glycogen, and nuclear and sarcoplasmic fragments. The liquid portion contains salts, extractives, and protein in true solution. When freed from the granules, the plasma is optically homogeneous, but on adding acid or heating to 55°, true precipitation of a dissolved muscle protein (myoprotein) occurs.

The fine plasma granules are degradation products from the muscular fibrils. They tend to flocculate spontaneously, and the so-called heat coagulation which occurs between 38° and 54° is due to rapid aggregation. Myoprotein is not completely coagulated by heat even at 80°; it is totally precipitated by dialysis. Tables of the composition and physical constants of muscle plasma are appended. The osmotic pressure is high, and the reaction always acid. The maximum production of acid substances occurs soon after the muscles are separated from the body, and it is these which cause the high osmotic pressure. The surface tension is also higher than that of blood-serum. W. D. H.

Fasting Studies. XI. Composition of Muscle from Fasting Dogs. HENRY C. BIDDLE and PAUL E. HOWE (*Biochem. Bull*, 1913, **2**, 386—389).—The tables given show an increase in water, and a decrease in nitrogen and creatine as a result of fasting. In the heart (one observation only) the nitrogen falls and the creatine rises. W. D. H.

Carnosine Content of the Muscles of Mammals. MARIE MAUTHNER (*Monatsh.*, 1913, **34**, 883—900).—The present investigation was undertaken with the object of deciding whether carnosine is the sole component of the carnosine fraction obtained by Gulewitsch (A., 1900, i, 516) from the muscles of mammals, and also in the hope of discovering an exact method for the estimation of carnosine. The following are the main conclusions:

(i) If a carnosine fraction is obtained from meat extract by addition of lead acetate and silver nitrate, separation of the precipitated matter, addition of silver nitrate and barium hydroxide to the filtrate and decomposition of the precipitate so obtained by means of hydrogen sulphide, it is frequently possible to separate the carnosine in the form of the sparingly soluble, blue, crystalline copper compound described by Gulewitsch. A quantitative separation is, however, never obtained, and there are many indications that, in addition to carnosine itself, a modification or decomposition product of it is often present which does not possess the power of dissolving copper hydroxide.

(ii) Estimations by the picrolonic acid method of the histidine obtained by hydrolysis of carnosine fractions by hydrochloric or sulphuric acids show that 80—90% of the nitrogen present in the latter is contained in the form of carnosine or of a closely allied compound.

(iii) The same result is obtained by the separation of the base from carnosine fractions in the form of a sparingly soluble, yellow, crystalline *picrolonate*, which, according to ultimate analysis and to the amount of picrolonic acid separable from it by addition of hydrochloric acid, is a mono-sodium compound of carnosinedipicrolonate, $C_{29}H_{29}O_{13}N_{12}Na$.   H. W.

The Occurrence of Alcohol-resistant Carmine-red and Brown-red Pigments in the Skin of Bony Fishes. EMIL BALLOWITZ (*Zeitsch. physiol. Chem.*, 1913, **86**, 215—218).—The red pigments referred to occur in the chromatophores, and are distinct from a yellow lipochrome which is soluble in alcohol.   W. D. H.

The Presence of Boron in Milk and Eggs. GABRIEL BERTRAND and HENRI AGULHON (*Compt. rend.*, 1913, **156**, 2027—2029. Compare A., 1910, ii, 241; 1912, ii, 854; this vol., i, 423).—From the very frequent occurrence of this element in animals and vegetables the authors raise the question as to whether the element may not play, like iron and manganese, an indispensable part (possibly catalytic) in the living cell. They have extended their investigation to milk (human, ass, goat, and cow) and to eggs (fowl, pigeon, wild duck, turkey, and goose), with distinct positive results in each case. Analysis indicates the presence of 0·08, 0·1, and 0·2 mg. of boron in 1 litre of human, ass's, and cow's milk respectively, and 1 mg. of boron in 1 kilogram of dried material from the egg of the fowl, turkey, or goose.   D. F. T.

The Alcohol Content of Milk after Ingestion of Alcohol and under the Influence of Tolerance. WILHELM VOLTZ and JOHANNES PAICHTNER (*Biochem Zeitsch.*, 1913, **52**, 73—95).—After a short period of toleration the amounts of alcohol appearing in the milk in the case both of cows, and of a woman, who ingested moderate quantities, are practically negligible. When cows are fed on residues from distillation processes, which seldom contain more than 0·1 to 0·3% alcohol, only, at the outside, a few milligrams .of alcohol can be ingested daily by infants fed on the milk from such animals, quantities, in fact, which are absolutely without action.   S. B. S.

Action of Hydrogen Peroxide on the Amylase of Human Milk. L. LAGANE (*Compt. rend.*, 1913, **156**, 1941—1943).—Starch paste is not liquefied by cow's or goat's milk before or after boiling, but a slight liquefaction occurs with either of these milks in a fresh state in presence of hydrogen peroxide. Fresh human milk, on the contrary, liquefies starch paste, and this action is greatly accelerated in presence of hydrogen peroxide, although the latter

does not enable boiled human milk to effect liquefaction. Similarly, the saccharification of starch paste by fresh human milk takes place more rapidly in presence of hydrogen peroxide, but this action is less marked than the acceleration of liquefaction. Control experiments of various kinds indicate that the acceleration is due to direct action of the peroxide on the amylase, or possibly to indirect action through peroxydases in the milk. T. A. H.

The Critical Solution Point of Urine. WILLIAM R. G. ATKINS and THOMAS A. WALLACE (*Biochem. J.*, 1913, 7, 219—230).—In normal urines the rise in critical solution point is about eight times as great as the depression of freezing point. In very dilute urines, and when excess of salts are present, this is greater; in the presence of dextrose or excess of urea it is less. The relationship between the rise of the critical solution temperature and the depression of the freezing point furnishes a useful datum in the examination of urine. W. D. H.

Toxic Bases in the Urine of Parathyroidectomised Dogs. W. F. KOCH (*J. Biol. Chem.*, 1913, 15, 43—63).—Digested proteins have a very toxic effect after parathyroidectomy; the toxic substances which arise either in intestinal or parenteral digestion pass into the urine, in which secretion several bases were found, among which β-amino-4-ethylglyoxaline, choline, and methylguanidine were identified. In animals in which no feeding occurred, the violent symptoms observed are attributed to disintegration of the body-protein. Histological examination reveals active degeneration of the cell-nuclei. The parathyroid secretion is regarded as concerned with anabolic processes closely related to the building up of nucleins. W. D. H.

The Chemical Composition of the So-called " Colloidal " Nitrogenous Substances obtained from Human Urine by Precipitation with Zinc Salts. H. THAR and J. BENESLAWSKI (*Biochem Zeitsch.*, 1913, 52, 435—438).—Salkowski has shown that alcohol produces a precipitation in concentrated human urine which contains nitrogen, is non-dialysable, and was supposed to consist of oxyproteic acid and similar substances. These same substances can also be obtained by precipitation with zinc sulphate. They have been investigated in greater detail by the authors, who now show that the precipitate contains chiefly uric acid and purine bases, contaminated with small quantities of urea, ammonia, and other constituents of the urine. S. B. S.

Acapnia and Shock. HENRY H. JANEWAY and EPHRAIM M. EWING (*Biochem. Bull.*, 1913, 2, 403—406).—The conclusion is drawn from experiments on dogs that the reduction of the carbon dioxide of the blood is not an important factor in the production of shock induced by hyper-respiration, but that the essential influence is an interference with the venous return to the heart. In experiments on the intestines, shock is due to manipulation of the gut, and not to

any lessening of carbon dioxide in the blood produced thereby. Aëration of the intestines without the addition of carbon dioxide does not produce shock.   W. D. H.

Beri-beri. VII. The Vitamine Fraction from Yeast and Rice Polishings. CASIMIR FUNK (*J. Physiol.*, 1913, **46**, 173—179).
—The vitamine fraction from yeast was separated into three substances: (1) with formula $C_{24}H_{19}O_9N_5$, (2) with formula $C_{20}H_{22}O_9N_5$, and (3) nicotinic acid. The first substance mixed with the third is stated to have some curative effect on pigeons suffering from polyneuritis.
The vitamine fraction from rice polishings was separated into two fractions: (1) with formula $C_{26}H_{20}O_9N_4$, and (2) nicotinic acid. The deductions as to their curative power are not yet published.
                                        W. D. H.

The Theory of Diabetes. I. Sarcolactic Acid in Diabetic Muscle. ROLLIN T. WOODYATT (*J. Biol. Chem.*, 1913, **14**, 441—451. Compare this vol., i, 559).—Muscles of glycogen-free animals form some sarcolactic acid (about 30% of the normal). This cannot come from glycogen, but must arise from preformed sugar or directly from amino- or fatty acids. The muscles of a severe human case of the disease formed even less than that of fully phloridzinised dogs. This suggests an impaired power to dissociate dextrose on the part of the muscles, as they are bathed in an abnormally high quantity of sugar. With D : N (dextrose : nitrogen) ratios of 3·65 : 1 post-mortem analyses of dog's muscles and livers show no glycogen. With ratios 2·8 or 3·0 : 1 this is not necessarily the case, and it cannot be assumed that with a constant D : N ratio of this magnitude an animal is free from glycogen.   W. D. H.

The Part Played by Acids in Carbohydrate Metabolism. II. Starvation Diabetes. HERBERT ELIAS and L. KOLB (*Biochem. Zeitsch.*, 1913, **52**, 331—361. Compare this vol., ii, 215).—The object of the investigation was to ascertain whether the diabetes produced by administration of carbohydrates during starvation is due to acidosis. This, from experiments on young dogs, appears to be the case for the following reasons. The starvation diabetes is accompanied by increased acidity of the blood, as determined by Spiro and Pemsel's method, and by an increased carbon dioxide tension in the alveolar air, as estimated by a modification of Wolffberg's technique The diabetes is always accompanied also by hyperglycæmia, which indicates that it cannot be ascribed to renal insufficiency; neither is it due to any action of the suprarenals, as it also occurs after bilateral splanchiotomy. Furthermore, the diabetes is depressed by administration of alkali, which also reduces the blood sugar to the normal. The diabetes appears to be due, therefore, to some disturbance in the intermediary metabolism, and is to a great extent to be ascribed to acidosis.   S. B. S

The Sugar Consumption in Normal and Diabetic (Depancreated) Dogs after Evisceration. JOHN J. R. MACLEOD and R. G. PEARCE (*Amer. J. Physiol.*, 1913, **32**, 184—199).—No differences occur in the consumption of sugar in the muscles and heart of depancreated dogs and normal dogs. This is opposed to the statements of Starling and Knowlton. W. D. H.

Gluconeogenesis. III. The Fate of *iso*Butyric, *iso*Valeric, and *iso*Hexoic Acids in the Diabetic Organism, with Consideration of the Intermediary Metabolism of Leucine and Valine. A. I. RINGER, EDWARD M. FRANKEL and L. JONAS (*J. Biol. Chem*, 1913, **14**, 525—538).—In experiments on phloridzinised dogs it was found that *iso*butyric acid and *iso*butyl alcohol give rise to dextrose, probably by undergoing demethylation and so giving rise to normal fatty acids (propionic acid). *iso*Valeric acid does not give rise to dextrose, but to large quantities of acetoacetic acid, acetone, and β-hydroxybutyric acid. *iso*Hexoic acid gives rise to dextrose, probably by demethylation to valeric acid and subsequent oxidation to propionic acid. In certain cases *iso*butyric acid possesses marked antiketogenic properties. It is suggested that *iso*valeric and *iso*butyric acids are normal intermediary products in the katabolism of leucine and valine respectively. W. D. H.

Gluconeogenesis. IV. The Fate of Succinic, Malic, and Malonic Acids in the Diabetic Organism, with Consideration of the Intermediary Metabolism of Aspartic Acid, Glutamic Acid, Proline, Lysine, Arginine, and Ornithine. A. I. RINGER, EDWARD M. FRANKEL and L. JONAS (*J. Biol. Chem.*, 1913, **14**, 539—550).—In phloridzinised dogs, succinic, malic, and perhaps malonic acids give rise to extra dextrose. Succinic acid is an intermediary substance in the metabolism of glutamic acid, ornithine, and proline, which accounts for their conversion into dextrose. Malonic acid may arise in part from the katabolism of aspartic acid; lysine in its katabolism may pass through a glutaric acid stage, which accounts for its non-conversion into dextrose. W. D. H.

Gluconeogenesis. V. The Rôle of Pyruvic Acid in the Intermediary Metabolism of Alanine. A. I. RINGER, E. M. FRANKEL and L. JONAS (*J. Biol. Chem.*, 1913, **15**, 145—152).—In phloridzinised dogs pyruvic acid is capable of yielding extra dextrose in the diabetic organism. In some cases the amount was much less than arises from similar amounts of alanine and lactic acid. Pyruvic acid cannot therefore be considered a necessary intermediary product in the conversion of alanine into lactic acid, and alanine cannot be considered to undergo oxidative deaminisation. W. D. H.

The Biochemical Relation between Pyruvic Acid and Dextrose. HENRY D. DAKIN and N. W. JANNEY (*J. Biol. Chem.*, 1913, **15**, 177—180).—Results similar to those obtained by Ringer (see preceding abstract). W. D. H.

The Influence of Thyroid- and Parathyroid-ectomy on Carbohydrate Metabolism. SOICHIRO- MIURA (*Biochem. Zeitsch*, 1913, **51**, 423—442).—The onset of alimentary galactosuria in cats is not markedly influenced either by unilateral thyroid or parathyroidectomy. Neither does this exert any influence on the sugar and nitrogen excretion in cases of phloridzin diabetes. Even, therefore, in an animal from which the thyroids and accessory glands have been extirpated, phloridzin causes new sugar formation at the expense of the proteins. Some weeks after the extirpation, however, the sugar/nitrogen ratio increases, as the nitrogen excretion sinks, and is not accompanied with a corresponding decrease of sugar formation. Adrenaline-glycosuria is markedly diminished in animals which have been deprived some weeks before of their thyroid glands and have been treated with phloridzin. S. B. S.

The Influence of Chloral Hydrate on Various Experimental Forms of Hyperglycæmia. AAGE TH. B. JACOBSEN (*Biochem. Zeitsch.*, 1913, **51**, 443—462).—In the case of rabbits, chloral hydrate causes hyperglycæmia, and increases hyperglycæmia produced by adrenaline, *piqûre*, and venesection. This increased action is most marked when the chloral exerts a strong narcotising action. In cases where the animals are only slightly influenced by the chloral, it is often impossible to state whether there has been an increase of hyperglycæmia or not. From the results it is impossible to determine whether the *piqûre* hyperglycæmia is due to adrenaline diabetes. S. B. S.

The Influence of Fever on the Elimination of Creatinine. VICTOR C. MYERS and G. O. VOLOVIC (*J. Biol. Chem.*, 1913, **14**, 489—508).—Fever increases creatinine excretion; so also in rabbits does artificial hyperthermia; hence the result is due to the rise of temperature which accelerates the normal metabolic processes. In toxic fevers, creatine is also generally found, but usually after the crisis. W. D. H.

Is Narcosis due to Asphyxiation? JACQUES LOEB and HARDOLPH WASTENEYS (*J. Biol. Chem.*, 1913, **14**, 517—523).—Chloral-hydrate, ethyl urethane, chloroform, and various alcohols produce complete narcosis in the fertilised eggs of the sea urchin, whilst they lower hardly at all the rate of oxidation in the egg. W. D. H.

Transformation of Calomel into Soluble Salts of Mercury in Digestive Media. H. ZILGIEN (*Compt. rend.*, 1913, **156**, 1863—1864).—Aqueous solutions of lactic acid, ammonia, or previously prepared ammonium lactate do not convert calomel into soluble salts of mercury; if, on the other hand, ammonia is added to a suspension of calomel in water containing lactic acid, a considerable quantity of soluble mercury salts is immediately formed, the amount of which does not increase when the mixture is preserved. A similar result is obtained with nascent ammonium

chloride, although the previously prepared substance is inactive. The soluble salt obtained is probably mercuric chloride. Sodium chloride, whether previously prepared or nascent, is inactive. Similar results are obtained with salts of bismuth, etc., so that probably a general principle is here involved.

In the dog the conversion of calomel into soluble salts of mercury occurs in the stomach only, mercuric sulphate being formed in the intestine. Administration of ammonia in suitable quantity causes a considerable increase in the amount of calomel transformed.

<div align="right">H. W.</div>

The Inactivation of the Hæmolytic Action of Ethyl Alcohol by Normal Serum Albumin. ALBERT FISCHER (*Biochem. Zeitsch.*, 1913, **52**, 60—72). — Normal serum inhibits hæmolysis by ethyl alcohol; sodium fluoride serum has a more powerful action in this respect than the serum which separates from a coagulum. Serum albumin also inhibits the hæmolytic action, the process being one of adsorption. Bases are strongly adsorbed by serum albumin, whereas with acids there is a negative adsorption.

<div align="right">S. B. S.</div>

The Mechanism of the Union of Digitalis-like Heart Poisons. VIKTOR WEIZSACKER (*Arch. expt. Path. Pharm.*, 1913, **72**, 347).—Merck's digitalin acts twenty-five times more strongly than strophanthin. The difference in activity of various preparations depends largely on the amount of active substances in combination, but the depression of cardiac activity depends on the concentration of the toxic molecules in the cell; combinations are formed in the cells.

<div align="right">W. D. H.</div>

The Distribution and Excretion of Digitoxin when Administered Subcutaneously to Bufo vulg. CAMILL LHOTÁK VON LHOTA (*Biochem. Zeitsch.*, 1913, **52**, 362—368).—In the case of the toad, digitoxin acts in the first instance as a nerve poison, and only as a heart poison when it is administered in large doses. When administered subcutaneously, it is for the most part absorbed, although a certain portion remains for a long time unabsorbed at the place of injection. The absorbed drug can be detected in the muscular tissue, in the cloacal fluid, and in the urine, in which about 10% of the substance administered is slowly excreted. The greater part of the absorbed drug cannot, however, be detected in the body, and appears to be destroyed. Keller's reaction was employed for the estimation of the digitoxin.

<div align="right">S. B. S.</div>

The Action of Ergotoxine. HENRY H. DALE (*J. Physiol.*, 1913, **46**, 291—300).—Ergotoxine does not reverse the motor effects of adrenaline by producing high tonus of plain muscle (blood vessels, uterus); it may even lower tone, and yet replace a motor adrenaline effect by an inhibitory one. Stimulation of the splanchnic nerves, after an adequate dose of ergotoxine, may cause a fall of blood-pressure although the suprarenal glands are removed.

Much of the paper is devoted to a discussion of the detection of sympathetic vaso-dilator nerves. There is no evidence apart from that furnished by the action of ergotoxine for a mixed motor-inhibitory supply to arteries in general. W. D. H.

[Physiological Action of] Certain Derivatives of Quinine. KNUD SCHROEDER (*Arch. expt. Path. Pharm.*, 1913, **72**, 361—386). —Towards Infusoria and Plasmodia, monobromoquinine and dibromoquinine are almost twice as strongly active as quinine; and dehydroquinine has about half the activity; the alkaloid, $C_{19}H_{22}O_3N_2Cl_2$, is inactive. These substances act in a similar relative way on bacteria, but not so strongly. Equimolecular doses of the quinine derivatives mentioned have the same antipyretic effect as quinine. They do not affect nitrogenous metabolism in rats, subcutaneous injection causes local necrosis, the various substances producing this in varying degrees. Dehydroquinine and quinine differ in so much as the vinyl group, $CH:CH_2$, of the quinine is changed into $C:CH$ in the first-named material; this alteration is believed to be responsible for the change in activity. W. D. H.

Action of Morphine on the Circulation. E. ANDERFS (*Arch. expt. Path. Pharm.*, 1913, **72**, 331—346).—In both dogs and rabbits morphine causes the heart to slow, although the arterial pressure may be unaltered or even slightly rise. In dogs this is due to central vagus stimulation; in rabbits there is, in addition, a peripheral stimulation due to decrease in negative intrapleural pressure Curare produces the same effect in rabbits, but in dogs, where it does not alter the intrathoracic pressure, there is no synergic action if both drugs are given together. W. D. H.

[Physiological Action of] Strophanthidin. A. GROBER (*Arch. expt. Path. Pharm*, 1913, **72**, 317—330).—Strophanthin acts in rabbits about 3·6 times as toxically as strophanthidin when given intravenously. Death is produced by both drugs by central respiratory paralysis. In minimal lethal doses, strophanthidin acts more quickly and instantaneously, whereas in the case of strophanthin death is preceded by dyspnœa, which lasts for some minutes. On the isolated frog's heart, both poisons act in the same concentration (1 in 1,500,000) in causing standstill of the ventricle. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Oxidation of Petroleum, Paraffin, and Benzene by Bacteria. NICOLAAS L. SÖHNGEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1145—1151).—Although most of the bacteria which oxidise hydrocarbons are unable to decompose fatty acids, some species

belonging to the mycobacteria are able to split fats by the secretion of lipase. Many species, such as *Bacillus fluorescens liquefaciens, B. pyocyaneus, Micrococcus paraffinae*, etc., were found in soil and canal water, and when cultivated in a medium containing tap water with 0·05% of ammonium chloride, 0·05% of dipotassium phosphate, and 1·0% of the hydrocarbon were able to oxidise the compound with great rapidity. Plate cultures showed the organisms to be extremely widely distributed, and it may rise to about 50,000 per gram of garden soil.

Pure cultures of the paraffin oxidising organisms decomposed, on an average, about 7·5 mg. of petroleum and 4 mg. of paraffin in twenty-four hours at 28° per square centimetre surface of the culture liquid. H. B. H.

A Comparative Study of the Metabolism of Pneumococcus, Streptococcus, Bacillus lactis erythrogenes, and Bacillus anthracoides. MARY LOUISE FOSTER (*J. Amer. Chem. Soc.*, 1913, **35**, 916—919. Compare this vol., i, 684).—A study of the proteolytic power of the various organisms. Two strains of *Pneumococcus* were very different in their power of affecting the protein molecule; increase of temperature from 37° to 40° favoured the reaction to such an extent that with the more active strain the phosphotungstic acid fraction was more than doubled, whilst the monoamine fraction is increased in the ratio 6 : 1. When milk was used as culture medium for *Streptococcus, Bacillus lactis erythrogenes*, and *B. anthracoides*, the liquid became alkaline and assumed a red colour and glue-like odour; no indication of lactic acid could be observed. The results indicate the probability of chemical similarity between organisms which morphologically are widely different. D. F. T.

Mechanism of the Acclimatisation of Yeasts to Formaldehyde. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1913, **156**, 1851—1852).—According to Effront, the acclimatisation of yeasts to formaldehyde is due to the destruction of the latter by an oxidising agent which develops in the yeast, the requisite oxygen being obtained from the air or from substances contained in the mixture; the substance produced by acclimatisation plays the part of selective catalyst, without which oxidation does not occur. The author considers this view to be improbable, and has carried out a series of experiments, in which he finds that (i) formaldehyde actually disappears, (ii) destruction takes place more readily in a medium rich in complex nitrogenous substances; if a poor barley wort is employed and the nitrogenous matter removed by means of tannin, fermentation becomes more difficult in the presence of a constant amount of formaldehyde; fermentation occurs more readily if a large initial quantity of yeast is used; (iii) combustion of formaldehyde is complete since formic acid cannot be detected; (iv) formaldehyde combines almost quantitatively with a wort rich in nitrogenous matter forming a labile compound, from which it can be recovered by energetic treatment. Fermentation, and conse-

quently acclimatisation, of the yeast are more difficult in proportion as the wort is poorer in organic nitrogen, and, with an artificial wort containing only ammonium phosphate, becomes very difficult.

The author is led to the conclusion that formaldehyde loses its antiseptic properties owing to the extreme ease with which it combines with groups containing nitrogen, and that the disappearance of the aldehyde corresponds simply with the consumption of the amino-compound formed by the yeast.   H. W.

The Formation of the Higher Alcohols from Aldehydes by Yeasts. I. The Conversion of Valeraldehyde into Amyl Alcohol. CARL NEUBERG and H. STEENBOCK (*Biochem. Zeitsch.*, 1913, 52, 494—503).—It has been already shown by Neuberg and his pupils that keto-acids can be converted by a ferment in yeasts into aldehydes. If these two classes of substances are intermediary products in alcoholic fermentation, it should be expected that the yeasts can convert aldehydes into alcohol. This is now experimentally shown to be possible, and yields of over 80% of the theoretical of amyl alcohol have been obtained from valeraldehyde when this aldehyde is present during alcoholic fermentation. The reaction is apparently a direct reduction, and not a conversion of aldehyde into an equal number of molecules of acid and alcohol by Cannizaro's reaction, as only small quantities of acid could be isolated, and the yield, furthermore, of the alcohol was too large to admit of this explanation. The higher alcohol was separated from the ethyl alcohol by fractional distillation.   S. B. S.

The Assimilability of Maltose by Yeasts. A. J. KLUYVER (*Biochem. Zeitsch.*, 1913, 52, 486—493).—It has been shown by Rose that certain yeasts will grow in culture media containing maltose, without producing fermentation, whereas they will not grow in dextrose solutions, although they will produce fermentation with this sugar when added to the medium containing maltose. These results were to a large extent confirmed by more extended researches of Lindner and Saito. The author now shows that certain yeasts will grow in Hayduck's medium containing some preparations of maltose, whereas they will not grow in the presence of maltose obtained from other firms. If, furthermore, the maltose samples which produce growth are purified by recrystallisation, they lose their power of producing growth. The results of Rose, Lindner, and Saito are therefore to be explained by the fact that the maltose they employed was not pure, but contained probably some protein substances derived probably from the diastase used in their preparation.   S. B. S.

The Protein Substances of Yeast. PIERRE THOMAS (*Compt. rend.*, 1913, 156, 2024—2027).—The only earlier work of an exact nature on this subject is that of Kossel (*Zeitsch. physiol. Chem.*, 1879, 3, 284; 1880, 4, 290) and of Schröder (A., 1902, i, 730). The author has succeeded, after partial autolysis of yeast, in isolating two protein substances; the first, which from its properties

appears to occupy a position between casein and the vitellin of egg-yolk, contains 16 2% nitrogen, 1·8% phosphorus, and 0·38% sulphur; it is soluble in dilute solutions of the alkali hydroxides and carbonates, but is precipitated by acids; rennet causes its coagulation, but less readily than it does caseinogen. If a solution of the protein in 1% sodium hydroxide is maintained at 37°, the phosphorus passes gradually into the mineral state, the extent of 58% being attained in five days (compare Plimmer and Scott, T., 1908, **93**, 1699).

The second substance, for which the author proposes the name *cerevisin*, closely resembles albumin; it is soluble in water, coagulable by heat, and not precipitable by acetic acid; the substance, which contains 16·3% nitrogen, 0·9% sulphur, and a trace of phosphorus, probably due to impurity, gives the usual precipitation and colour reactions.   D F. T.

Rôle of Reductase in Alcoholic Fermentation   S. D. Lvov (*Bull Acad. Sci. St. Pétersbourg*, 1913, 501—532).—Further experiments on the lines of those previously carried out by Palladin and the author (see this vol., i, 684) lead to the following results

The first stage, or one of the first stages, in alcoholic fermentation consists in the activation of two atoms of hydrogen with the aid of reductase. So far as is at present known, this active hydrogen may be formed either directly from the dextrose or as the result of the ionic dissociation of water; in the latter case the dextrose would be oxidised by the hydroxyl ions, whilst in the former this early stage would be represented by the equation

$$C_6H_{12}O_6 + R = (C_6H_{12}O_6 - 2H) + RH_2,$$
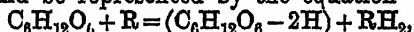
where R denotes the reductase. The hydrogen fixed temporarily on the reductase is necessary to the further course of normal fermentation. Failure of the distillate to yield the reaction for aldehydes with magenta and sulphurous acid indicates that the formation of aldehydes during the fermentation of sugar, if it actually occurs, is a more complex process than is assumed in Kostytschev's scheme (A , 1912, ii, 589, 860; this vol., i, 323).

Between the reducing and fermentative capacities of yeast strict parallelism is observed; the reductase gives up the hydrogen it fixes to an amount which stands in equimolecular relation to the diminution in yield of the products of fermentation.

A number of auto-fermentation experiments have also been made. The results of these show that the extraction during the process of reduction, of 2 gram-atoms of hydrogen by 1 gram-mol of methylene-blue, is accompanied by the evolution of an excess of 1 gram-mol of carbon dioxide   Hence a fermenting medium contains some substance which. in absence of sugar, is capable of liberating 1 mol of carbon dioxide when the conditions are such that the substance itself loses 2 atoms of hydrogen   This process is found to be enzymic in character, and is one-sided in that no corresponding excess is observed in the yield of alcohol. The excess of carbon dioxide is regarded as resulting from the decomposition of amino-acids, with parallel formation of aldehydes.

The conclusion is drawn that activation of the hydrogen under the influence of reductase is an all-important factor in the processes of fermentation, which are unable to take place in absence of reductase.   T. H. P.

Alcoholic Fermentation of Sugar. EDUARD BUCHNER and KURT LANGHELD (*Ber.*, 1913, 46, 1972).—Sugar was allowed to ferment with expressed or macerated yeast juice in presence of trisodium phosphate or disodium hydrogen phosphate in an extraction apparatus, through which a flow of ether was maintained. The presence of acetaldehyde in the solvent was detected by the formation of the *p*-nitrophenylhydrazone. A similar result was obtained by Kostytschev in the presence of zinc chloride (A., 1912, ii, 589).   J. C. W.

Alcoholic Fermentation. IV. Decomposition of Sugar by Dry Yeast in Presence of Zinc Chloride. S. KOSTYTSCHEV and A. SCHELOUMOV (*Zeitsch. physiol. Chem.*, 1913, 85, 493—506. Compare A., 1912, ii, 589, 860; 1913, i, 323, 434).—When sugar is fermented by yeast preparations in the presence of zinc chloride, the normal series of changes is disturbed and acetaldehyde formed. Parallel with this there is a marked restriction of the production of carbon dioxide. Various zinc salts act in a similar manner, most acetaldehyde being produced in presence of zinc iodide, bromide, or chloride, and less when zinc acetate, carbonate, or phosphate is used.

In the absence of zinc chloride, equal quantities of carbon dioxide and alcohol are obtained on fermentation, but after twenty-four hours about 25% of the sugar decomposed has not been converted into these products; it has probably been used to form hexose phosphate. After forty-eight hours' action, the whole of the sugar is converted into alcohol and carbon dioxide. In parallel experiments in which 0·15 gram of zinc chloride was added per 10 grams of yeast, the sugar is more rapidly decomposed, the fermented part of it being used to form other products. At first the amounts of carbon dioxide and alcohol are equal; after forty-eight hours the production of carbon dioxide is in excess.

When the amount of zinc chloride is doubled, a still larger proportion of the sugar decomposed is not fermented. With 1·2 grams of zinc chloride to 10 grams of yeast, no action takes place.

In a similar manner the addition of 0·5 gram of methylene-blue affects the fermentation. Only two-thirds of the sugar decomposed is fermented, although carbon dioxide and alcohol are produced in equal proportions. The fermentative energy is decreased.

The experiments indicate that the two end-products of fermentation are not formed simultaneously. Alcohol is partly replaced by acetaldehyde.   E. F. A.

Alcoholic Fermentation. V. Decomposition of Protein by Dry Yeast in Presence of Zinc Chloride. S. KOSTYTSCHEV and W. BRILLIANT (*Zeitsch. physiol. Chem.*, 1913, 85, 507—516. Compare preceding abstract).—Generally speaking, external factors act in

an opposite manner towards zymase fermentation and protein decomposition by yeast.

In the absence of sugar, zinc chloride very slightly accelerates the auto-decomposition of dry yeast protein. In the presence of sugar the reverse is the case, the proteolysis being slightly retarded, no doubt owing to the presence of the sugar and the acetaldehyde formed from it. In concentrated sugar solutions the retardation is more marked.

The retardation of the zymase fermentation by zinc chloride is thus not due to acceleration of the antagonistic proteolysis, but to a direct action on the zymase.   E. F. A.

Nitrogen Metabolism in Aspergillus niger. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1047—1057).—When grown in nutrient solution containing ammonium salts and dextrose or lævulose, the mould is found to give a high nitrogen : carbon ratio. This is attributed not to a simple adsorption of the nitrogen compound, but to its assimilation and immediate transformation into compounds insoluble in hot distilled water.

With increasing age the nitrogen : carbon ratio falls rapidly, and then remains practically constant.

An excretion of ammonia is observed, and this occurs irrespective of the nitrogen compound supplied; nitrate is reduced to ammonia, but not to free nitrogen. The addition of manganese salts increases the velocity of metabolism, whilst the substitution of rubidium for potassium in the nutrient solution is without effect. Where the amount of nitrogen is limited, there did not appear to be any assimilation of atmospheric nitrogen.

H. B. H.

Phosphorus Metabolism in Aspergillus niger. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1058—1063).—The ratio of phosphorus to assimilated carbon in old cultures was found to be constant. In the early stages of growth comparatively large quantities of phosphorus are taken up, but, in contradistinction to the same stage in nitrogen assimilation, this phosphorus does not appear to be transformed into organic compounds, such as lecithin or phytin, and can consequently be extracted with hot water. A retardation in spore-formation may be induced by the addition of excess quantities of phosphorus salts.

H. B. H.

Cleavage of Pyromykuric Acid by Mould Enzymes. ARTHUR W. DOX and RAY E NEIDIG (*Bioch,m. Bull.*, 1913, **2**, 407—408).— Various moulds cleave hippuric acid, and the products can be determined by Sörensen's formaldehyde method. If the synthesis of hippuric acid from benzoic acid in the body is due to an enzyme, the synthesis of corresponding derivatives from substituted benzoic acids may be attributed to the same cause, but there is no reason to suppose that a separate enzyme is necessary for each. This reasoning may be extended to analogous compounds, in which a

heterocyclic replaces the benzene nucleus. In the present experiments, in which pyromykuric acid was subjected to the influence of moulds, the cleavage produced was comparatively small, but this is no evidence that the enzyme is a specific one.   W. D. H.

Importance of Oxygen in the Germination of Peas. VL. P. MALTSCHEVSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 639—664).— The results of experiments on the germination of peas under various conditions bring out the following points.

In the case of living seeds, the action of oxygen in causing germination cannot be replaced by that of methylene-blue. The initial influence of the air in stimulating resting seeds under anærobic conditions is of great importance, and changes the character of the anærobic development of carbon dioxide. The alcoholic fermentation produced by seeds under strictly anærobic conditions is accompanied by another process, which leads to the evolution of carbon dioxide from another source, but furnishes no alcohol. Such process is apparently peculiar to living seeds, and is lacking or, at any rate, greatly enfeebled with dead seeds. In the investigation of the anærobiosis of seeds, it is essential to deprive the latter of oxygen even in the first stages of steeping. For the initiation of the germination of peas, absorption of atmospheric oxygen is necessary, not merely for supplying the energy liberated by the oxidation of substances existing in the resting seeds, but also for the formation of new compounds.   T. H. P.

Assimilation of Iron by Plants. WILHELM VAUBEL (*Chem. Zeit.,* 1913, **37**, 737).—Iron and ammonium nitrate interact with production of ferrous oxide, ferric hydroxide, and a small amount of a soluble compound, $Fe_2O_4(NO \cdot NH_4)_2$, or $Fe_2O_6(NO \cdot NH_4)_3$ (*ibid.*, 637; Kaufmann, A., 1901, ii, 554). It is suggested that iron is taken up by plants partly in this form. The compound only exists in solution, and decomposes when the solution is evaporated down. According to the concentration, the solution is colourless or dark grey; if yellow, ferric nitrate is present.   N. H. J. M.

The Oxidative Formation of Nitrous Acid in Extracts of Plants. ALEXIS BACH (*Biochem. Zeitsch.*. 1913, **52**, 418—422).— The author confirms the observation of Mazé, that nitrous acid is formed in plant extracts when exposed to the action of air. The nitrous acid thus produced is spontaneously destroyed. Nitrous acid is formed only in traces, if the extract is first heated. Reasons are given for assuming that nitrous acid is formed from the amino-acids present and not from nitrates, and against the assumption that the formation of iodine from potassium iodide is not due to the presence of nitrous acid, but is due directly to the existence of an oxydase in the tissues.   S. B. S.

Relationship of Bases and Mineral Acids in Plant Tissues. GUSTAVE ANDRÉ (*Compt. rend.*, 1913, **156**, 1914—1916).—In connexion with Warington's observation (A., 1900, ii, 569), that crops

usually show a deficiency of bases on the assumption that all the nitrogen enters the plant in the form of nitrates, the author points out that this is the case for barley (A., 1912, ii, 675, 803) and for linseed (A., 1913, i, 688), but not for spurrey (*loc. cit.*). In the last case the bases are in excess.   T. A. H.

Detection of Urea in Plants. ROBERT FOSSE (*Compt. rend.*, 1913, **156**, 1938—1941. Compare A., 1912, ii, 1203; 1913, i, 432). —Some objection might be taken to the work already done on this subject (*loc. cit.*) owing to the fact that the plant preparations in which urea was detected had been concentrated by heat in presence of acetic acid. The author has therefore repeated and extended the work by operating on plant preparations obtained by expression or maceration in the cold. From such products the xanthhydrol derivative of urea is readily precipitated. Urea has thus been detected in the following plants: *Aspergillus niger*, *Penicillium glaucum*, carrot, potato, spinach, endive, chicory, turnip, green haricot, peas, purslane, lettuce, pumpkin, maize grain, and in the embryos of wheat, rye, sunflower, beet, field-bean, lucerne, lentil, lathyrus, grain, pumpkin, horse-bean, dwarf-bean, *Trifolium incarnatum*, and common haricot. Examples of the three methods used in preparing the extracts are given.   T. A. H.

The Detection of Formaldehyde in Plants. HEINRICH FINCKE (*Biochem. Zeitsch.*, 1913, **52**, 214—225).—For these researches, the Grosse-Bohle reagent for the detection of formaldehyde was employed. This consists of a rosaniline salt in the presence of sulphites and free hydrochloric acid, and is to be distinguished from the ordinary magenta-sulphite solution for detection of aldehydes, by the presence of free mineral acid. It was found by the author to be capable of detecting formaldehyde in the dilution 1 in 500,000, giving with the aldehyde a violet colour. In numerous experiments on plants, no indication of the presence of formaldehyde was obtained with the use of this reagent; furthermore, formaldehyde could not be detected by the reagent after addition to certain living plants. The author draws the conclusion that his investigations throw no light on the correctness or otherwise of Bayer's assimilation hypothesis.   S. B. S.

The Reduction Ferments. IV. Vegetable Perhydrases. ALEXIS BACH (*Biochem. Zeitsch.*, 1913, **52**, 412—417).—It has been shown by the author that animal tissues contain a perhydrase which can reduce nitrates to nitrites in the presence of aldehydes. The existence of a similar vegetable ferment is now demonstrated, which can be obtained from potatoes by extraction with water and filtration of the extract. If this extract is kept under antiseptic conditions (in the presence of sodium fluoride) and in the absence of air, a co-ferment is gradually produced, which can replace the aldehyde in the above-described perhydrase reaction. The co-ferment which activates the animal perhydrase, and which is obtained by extraction of animal tissues by hot water, will not

activate the vegetable perhydrase, which also differs from the animal perhydrase in that it will not reduce methylene-blue. It has not yet been found possible to replace the co-ferment in the vegetable perhydrase reaction with amino-acids or keto-acids, and its exact nature is still undetermined. S. B. S.

Arsenic and Manganese in Young and Old Leaves. F. JADIN and A. ASTRUC (*Compt. rend.*, 1913, **156** 2023—2024. Compare A., 1912, ii, 478, 976).—The observation of Pichard (A., 1899, ii, 40) that manganese appears to become concentrated in those parts of a tree which are in vegetative activity, appears to depend for its correctness on the method of analysis.

According to their age, the different organs contain variable proportions of water and of mineral matter. The experimental results indicate that the amounts of arsenic and manganese in the old leaves of various trees examined are decidedly greater than in the young leaves, if the percentage is calculated on the weight of the fresh leaves. The difference becomes less marked if the percentage of the elements is referred to the dried organs, whilst if the percentages are calculated on the ash the case is actually reversed. D. F. T.

Variation of Carbohydrates in Leaves During Development. E. MICHEL-DURAND (*Compt. rend.*, 1913, **156**, 1926—1929. Compare Combes, A., 1909, ii, 426).—The author has determined the dry weight, reducing and non-reducing sugars, glucosides, dextrin, starch, non-nitrogenous extractive matter, amyloids, and cellulose in the leaves of *Fagus sylvatica*, *Ampelopsis hederacea*, and *Betula alba*, at various stages of development during the year. The results for *Betula alba* leaves are quoted in full in the original. The following conclusions are drawn from the whole of the results. There is a general diminution in carbohydrates towards the end of the season. After attaining a maximum dry weight in August to September, the leaves lose weight until and after they fall. The leaves of *Fagus* and *Betula* contain the maximum amount of reducing sugars when yellow; those of *Ampelopsis* when red; these are corresponding states, and after these stages the amount diminishes rapidly. Starch, when it exists, reaches a maximum while the leaves are green, and then diminishes gradually; yellow leaves contain only traces, but in *Fagus* it persists in the dead leaves until these are dry. Amyloids are at a maximum in *Betula* leaves when these are yellow, but in *Ampelopsis* leaves while they are still green. Cellulose diminishes steadily in *Ampelopsis* leaves, but increases steadily in *Betula* leaves. Rain and dew carry off some soluble carbohydrates from dead leaves. The diminution of carbohydrates in leaves as the season's growth proceeds is due partly to migration of these substances into the stem, partly to respiration, and partly to the effect of atmospheric water. The formation of soluble sugars towards the end of the season is favoured by low temperatures. T. A. H.

Organic Chemistry.

Formation of Methane by Catalysis, Starting with Carbon Monoxide and Water Vapour. Léo Vignon (*Compt. rend.*, 1913, **157**, 131—134. Compare A., 1911, i, 101; ii, 391).—An examination of the effect of the metals iron, nickel and copper, and the oxides of aluminium, magnesium and silicon as catalysts, at temperatures varying from 250° to 1250°, in the formation of methane from carbon monoxide and water vapour. They are all effective, but to a variable degree, nickel being the most active at 600°. The mechanism of the action is different for the various catalysts. In all probability iron and the oxides of aluminium and silicon act through the intermediate formation of a carbide, which is decomposed by the water vapour as fast as it is formed. W. G.

Pyrogenetic Decomposition of the Butadiene Hydrocarbons. Hermann Staudinger, R. Endle, and J. Herold (*Ber.*, 1913, **46**, 2466—2477).—Isoprene when passed through a tube heated at 750° is converted to the extent of 45—55% into a tar, which in appearance and composition closely resembles coal tar, and contains benzene, toluene, naphthalene, a-methylnaphthalene, anthracene, chrysene, etc. The rest of the isoprene is converted into butadiene and into hydrogen, methane, ethylene, or into retort carbon.

At 400° under similar treatment isoprene is partly unattacked, and partly polymerised to unsaturated hydrocarbons—terpenes. Very little gas is formed, but there is some amylene and β-methyl-Δ^{β}-butylene produced.

At 600—700° a mixture of unsaturated hydrocarbons results, which no longer contains terpenes, but resembles crude petroleum. At temperatures above 700°, aromatic compounds are formed; at 750° they are almost entirely, and at 800° they are, the only products.

At 700°, but in a vacuum of 20—25 mm, almost half the isoprene remains unchanged. Unsaturated compounds are formed, but no tar.

When isoprene or butadiene is prepared by pyrogenetic reactions it is advisable to work in a vacuum and to cool rapidly if a high yield is desired.

Isoprene is primarily condensed to hydroaromatic compounds. These polymerise further, or condense with isoprene to form substances which decompose into aromatic compounds, the side-chains being eliminated. The formation of the tar from acetylene and ethylene derivatives, which might have been formed primarily by the pyrogenetic decomposition of isoprene, is improbable, since these compounds are not formed at the lower temperatures, or on heating in a vacuum.

Butadiene may originate from the hydroaromatic substances or from amylene.

β-Methyl-Δ^{β}-butylene at 750° gives rise to butadiene, but this is obtained in much larger quantity on decomposing amyl alcohol. The alcohol yields relatively little tar; β-methyl-Δ^{β}-butylene gives a considerable quantity. In this case also hydrogen is separated from carbon, and there is no scission of carbon linkings with the formation of methane.

Butadiene also takes part in the formation of the aromatic tar, but it polymerises more slowly than isoprene, and the amount of tar products formed is therefore less.

Dimethylbutadiene behaves just as isoprene does at high temperatures, forming tar and small quantities of butadiene at 800°.

It is considered that the polymerisation of butadiene hydrocarbons plays only a small part in the formation of tar from coal. The tar is mainly formed by the dehydrogenation or decomposition of hydroaromatic substances.　　　　　　　　　　　　　　　　　E. F. A.

The Action of Sodium in Liquid Ammonia on the True Acetylenic Hydrocarbons of the Fatty Series, and a Method of Formation of Ethylenic Hydrocarbons. PAUL LEBEAU and MARIUS PICON (*Compt. rend.*, 1913, **157**, 137—139).—Sodium in liquid ammonia reacts with the acetylenic hydrocarbons of the fatty series quantitatively, giving the sodium derivative of these hydrocarbons (2 mols.) and the corresponding ethylenic hydrocarbon (1 mol.) according to the equation :

$$3C_3H_4 + 2NaNH_3 = 2C_3H_3Na + 2NH_3 + C_3H_6.$$

The products of the reaction are pure, and no secondary reactions were noticed.　　　　　　　　　　　　　　　　　W. G.

Ethylenic Isomerism of s-Dibromoethylene. H. VAN DE WALLE. (*Bull. Soc. chim. Belg.*, 1913, **27**, 209—217).—Crude s-dibromoethylene is best obtained in quantity by the action of zinc on an alcoholic solution of tetrabromoethane. It boils at 108—112°, and the two isomerides cannot be separated by fractional distillation on account of the spontaneous reversion of the different fractions to the equilibrium mixture. Attempts to separate them by fractional solidification and also by fractional precipitation by water of a solution of the crude bromo-derivative in acetic acid were unsuccessful. Their isolation can be effected, however, by taking advantage of the fact that each isomeride forms a binary mixture with alcohol. By repeated fractionation of a solution of the crude substance in absolute ethyl alcohol with careful exclusion of moisture, two binary mixtures can be isolated. The first of these has b. p. 75·6—75·9°/760 mm., and contains 64% of s-*dibromoethylene*, m. p. −6·5°. The second has b. p. 77·7—78°/760 mm., and contains 32·5% of s-*dibromoethylene*, m. p. −53°. The pure compound, m. p. −6·5°, has b. p. 108°, $D_4^{17\cdot5}$ 2·2667, $n_{H\alpha}^{17\cdot5}$ 1·54563, $n_D^{17\cdot5}$ 1·55054, $n_{(\gamma)}^{17\cdot5}$ 1·57381, whilst the other isomeride has b. p. 112·5°, $D_4^{17\cdot5}$ 2·2846, $n_{H\alpha}^{17\cdot}$ 1·53837, $n_{H\alpha}^{1\cdot}$ 1·53791, $n_D^{17\cdot}$ 1·54312, $n_D^{18\cdot}$ 1·54256, $n_G^{18\cdot5}$ 1·55406. Slight errors are probably involved in the determination of the density owing to rapid isomerisation which occurs with such facility that an equilibrium mixture is formed in the course of a few hours. On exposure to air and moisture, the dibromocompounds are readily decomposed with evolution of hydrogen bromide.

The equilibrium mixture of the two isomerides has $D_4^{17\cdot5}$ 2·2788, $n_{H\alpha}^{17\cdot5}$ 1·54092, $n_D^{17\cdot5}$ 1·54560, and thus contains about 33·5% of the modification, m. p. −6·5°.

The compounds are readily decomposed by alcoholic potassium

hydroxide according to the equation :

$$C_2H_2Br_2 + KOH = C_2HBr + KBr + H_2O,$$
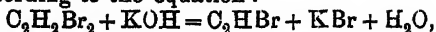
the isomeride, m. p. −53°, being by far the more readily decomposable. **H. W.**

An Application of Young's Method for the Preparation of Absolute Alcohol. GEORGES CHAVANNE (*Bull. Soc. chim. Belg.*, 1913, 27, 205—209).—The author criticises Young's method of dehydrating aqueous alcohol by means of benzene, and has examined the effect of substituting s-dichloroethylene for the latter substance. The general course of the process is similar in each case. s-Dichloroethylene, b. p. 48·35°, yields with aqueous alcohol a ternary mixture, b. p. 44·4°, which has the composition, s-dichloroethylene 94·5%, alcohol 4·4%, water 1·1%. The binary mixture of s dichloroethylene and alcohol has b. p. 46·5° and contains 94·0% of the former, whilst the binary mixture of s-dichloroethylene and water, containing 98·1% of the former, has b. p. 45·3°. With the isomeric s-dichloroethylene, b. p. 60·25°, the ternary mixture has the composition, s-dichloroethylene 90·5%, alcohol 6 65%, water 2·85%, and b. p. 53·8°. The binary mixture of s-dichloroethylene and alcohol, containing 90·2% of the former, has b. p. 57·7°, whilst the corresponding mixture of s-dichloroethylene and water contains 96·65% of the former and has b. p. 55·3°. The following are the main conclusions :

(i) The loss of alcohol due to the formation of a ternary mixture is rather greater than when benzene is used if the isomeride, b. p. 48·35°, is employed, rather less in the case of the isomeride, b. p. 60·25°. The use of a mixture of equal weights of the two isomerides, corresponding approximately with commercial s-dichloroethylene, leads to a slightly greater loss of alcohol than is the case with benzene, whilst the employment of the equilibrium mixture gives results practically identical with those obtained with the aid of benzene.

(ii) In practice, a portion of the alcohol would also be removed in the form of a binary mixture. Such loss, however, would be less serious than that encountered when benzene is used, since the binary mixtures of alcohol and s-dichloroethylene are poorer in alcohol than the corresponding mixtures of alcohol and benzene.

(iii) The use of the dichloro-derivatives has the advantage that the b. p. of alcohol is 20·6° higher than that of the least volatile binary mixture. In this respect, the dichloro-derivatives are superior to benzene or n-hexane.

The author is led to the conclusion that the above method is not suited to the commercial preparation of absolute alcohol, since the losses are much greater than those involved by the use of lime.

H. W.

Composition of Certain Formates. CHARLES H. HAMPSHIRE and W. R. PRATT (*Pharm. J.*, 1913, 91, 138—142).—An examination of commercial specimens of the principal formates and an investigation of the methods of preparation gave the following results : Sodium formate sometimes consists of the anhydrous salt and sometimes of crystals of the dihydrate. Ferric formate has the formula,

$$Fe_3(OH)_2(HCO_2)_7,4H_2O,$$
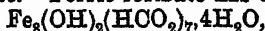
assigned to it by Belloni (A., 1909, i, 283), and not $Fe_2(HCO_2)_6,H_2O,$

as stated in the B. P. Codex. Magnesium formate has the formula $Mg(HCO_2)_2,2H_2O$, and calcium formate the formula $Ca(HCO_2)_2$. Quinine formate is not anhydrous, but has the composition

$$C_{20}H_{24}O_2N_2,HCO_2H,H_2O.$$
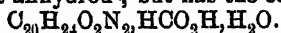
When freshly prepared, strychnine formate contains $2H_2O$, but it effloresces quickly.   W. P. S.

Esters of Palmitic Acid. MARJORY STEPHENSON (*Biochem. J.*, 1913, **7**, 429—435).—Palmityl chloride, a colourless oil, b. p. 198—200°/15 mm., condenses with glycol in presence of pyridine with chloroform as a solvent to *ethylene dipalmitate*, $(C_{15}H_{31}\cdot CO_2)_2C_2H_4$, which crystallises in rosettes of fine needles, m. p. 65° (corr.).

Glyceryl tripalmitate (tripalmitin), prepared in a similar manner, crystallises in colourless, fine needles, m. p. 62° (corr.).

Mannityl hexapalmitate crystallises in rosettes of fine needles, m. p. 64·5° (corr.).

Dextrose pentapalmitate,

$$C_{15}H_{31}\cdot CO_2\cdot CH_2\cdot[CH\cdot O\cdot CO\cdot C_{15}H_{31}]_4\cdot CHO,$$

has m. p. 62°.   E. F. A.

The Action of Complex-forming Acids or their Salts on Platinum Ammonia Compounds. II. Reactions with Ethylthiolacetic Acid. LUDWIG RAMBERG (*Ber.*, 1913, **46**, 2353—2362. Compare this vol , ii, 607).—An intermediate product of the action of ethylthiolacetic acid on *cis*-dinitratodiammineplatinum is *nitrato-diammineplatinum ethylthiolacetate*, $Pt(NH_3)_2(NO_3)(CO_2\cdot CH_2\cdot SEt)$, which crystallises in large, colourless prisms, m. p. 188—189°. When distilled with dilute sodium hydroxide only one half of the ammonia is liberated. When, however, ethylthiolacetic acid is added to dissolve the compound and then, after an interval, it is distilled with sodium hydroxide, the whole of the ammonia is set free. When the above nitratodiammineplatinum ethylthiolacetate is boiled with concentrated acetic acid one molecule of ammonia is liberated, and *nitratomonammineplatinum ethylthiolacetate*, $CH_2\!\!<^{CO\cdot O}_{SEt}\!\!>P\!\!<^{NO_3}_{\cdot NH_3}$, is obtained. This crystallises in large, flat, colourless prisms, grouped in rosettes, m. p. 193—194° (decomp.).

On shaking *cis*-dinitritodiammineplatinum with an aqueous solution of ethylthiolacetic acid in a closed tube only a little dissolves, and some nitrous fumes are liberated on opening the tube. If, however, sodium ethylthiolacetate is substituted for the free acid and the mixture is boiled in an open vessel, the main product is *sodium dinitrito-(bisethylthiolacetato)-platinoate*, $(CO_2Na\cdot CH_2\cdot SEt)_2Pt(NO_2)_2,2H_2O$, which is also obtained on adding sodium nitrite to α-platinoethylthiolacetate; it forms small, colourless crystals.

trans-Dichlorodiammineplatinum reacts with ethylthiolacetate to form a colourless, complex substance of the composition

$$Pt_2(NH_3)_4Cl_3(CO_2\cdot CH_2\cdot SEt)(CO_2H\cdot CH_2\cdot SEt),$$
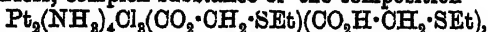
which evolves ammonia only slowly when distilled with sodium hydroxide, and decomposes on boiling with acetic acid into *trans*-dichloro-

diammineplatinum, *trans*-diammineplatinum bisethylthiolacetate, and ethylthiolacetic acid. Hence the formula given should probably be doubled.

Ethylthiolacetic acid combines with *trans*-dinitratodiammine-platinum to the compound $Pt(NH_3)_2(NO_3)_2 2CO_2H\cdot CH_2\cdot SEt, H_2O$; this crystallises in colourless rosettes of prismatic crystals, m. p. 115—116°.

Ethylthiolacetic acid and *trans*-sulphatodiammineplatinum combine to form the *additive product*, $Pt(NH_3)_2SO_4, 2CO_2H\cdot CH_2\cdot SEt$, which crystallises in colourless tablets or prisms. It reacts with potassium platinochloride, K_2PtCl_4, forming platinoethylthiolacetate, which reacts with hydrogen chloride, forming *monochloro-(bisethylthiolacetato)-platinoic acid*, $(CO_2H\cdot CH_2\cdot SEt)PtCl(CO_2\cdot CH_2\cdot SEt)$, and *trans*-dichloro-diammineplatinum, $Pt(NH_3)_2Cl_2$. The former compound crystallises in greenish-yellow aggregates, m. p. 166—167°.

The above sulphate reacts with barium hydroxide, yielding colourless, microscopic needles of *trans*-diammineplatinum bisethylthiol-acetate, which can also be obtained from the corresponding iodide on boiling with silver ethylthiolacetate. It has m. p. 200—203° (decomp.).

trans-Dinitritodiammineplatinum and sodium ethylthiolacetate react very slowly, yielding the same sodium dinitrito-(bisethylthiolacetato)-platinoate as was derived from the *cis*-derivative. E. F. A.

Lactonisation of α-Ketonic Esters. HENRI GAULT (*Compt rend.*, 1913, 157, 135—137. Compare A., 1911, i, 709).—By a study of its compounds with hydrazine and ammonia the author has definitely established the constitution of the neutral substance, b. p. 176—177°/13 mm., obtained by saturating ethyl pyruvate with hydrogen chloride in the cold, as being the ethyl ether of the enolic form of ethyl α-keto-γ-valerolactone-γ-carboxylate,

$$CO_2Et\cdot CMe {<}^{O--CO}_{CH:C\cdot OEt}$$
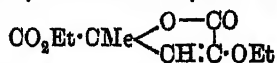
(compare A., 1912, i, 237). It unites with hydrazine (1 mol.) to form the *lactone hydrazide*, $NH_2\cdot NH\cdot CO\cdot CMe{<}^{O--CO}_{CH:C\cdot OEt}$, m. p. 146°, and a small quantity of a crystalline *compound*, m.p. 230° (decomp.), is obtained at the same time. With excess of hydrazine it gives the *hydrazinolactone hydrazide*, $NH_2\cdot NH\cdot CO\cdot CMe{<}^{O--C(OH)\cdot NH\cdot NH_2}_{CH:C\cdot OEt}$, m. p. 180° (decomp.).

Ammonia reacts similarly in the cold, giving an *amide*, m. p. 190°, and a second *compound*, m. p. 245° (decomp.).

The compound, m. p. 230°, obtained in the action with hydrazine (1 mol.) and the compound, m. p. 245°, obtained in the action with ammonia are shown to be derivatives of ethyl α-chloro-γ-keto-α-methyl-glutarate, formed during the aldolisation of the pyruvic ester.

W. G.

Catalytic Preparation of Ketones Over Oxides of Iron. ALPHONSE MAILHE (*Compt. rend.*, 1913, **157**, 219—221).—Both ferrous and ferric oxides can replace cadmium oxide (compare this vol., i, 828) as catalysts in the preparation of simple or mixed ketones from their acids. The oxides are kept at a temperature of 430—490°. The acids employed may be aliphatic or aromatic, or mixtures of the two, and, as in the case of cadmium oxide, *iso*valeric and *iso*butyric acids give the worst yields. The yields are given for numerous ketones.

W. G.

The Mechanism of the Formation of Acrose. ERNST SCHMITZ (*Ber.*, 1913, **46**, 2327—2335).—At the time of their identification of α-acrose as *dl*-fructose, Fischer and Tafel suggested that the accompanying β-acrose present in smaller amount in the product from dibromopropaldehyde and from glycerose was a sugar probably allied to sorbose. From the occurrence of a ketose it is obvious that the process cannot be a simple aldol condensation of glyceraldehyde, but that at some stage of the change an aldehyde group must become transformed into a ketonic one; this probably occurs in the triose molecule, as the conditions of the condensation are not such as to cause a rearrangement in the hexose molecule; it has also been shown (Wohl and Neuberg, A., 1901, i, 12) that the trioses are easily interconvertible under these conditions, because whether aldehyde-free glycerose or pure glyceraldehyde is applied for the condensation, β-acrose is always produced.

By the condensation of pure glyceraldehyde, obtained conveniently by the hydrolysis of the corresponding acetal with N/10-sulphuric acid and subsequent treatment with baryta, under the influence of 0·1% excess of baryta at the ordinary temperature, a solution was obtained which yielded a crystalline mixture of two hexoses; this could be separated by recrystallisation from hot methyl alcohol; the less soluble constituent, needles, m. p. 129—130°, D^{16} 1·665, osazone n. p. 216—217°, was *dl*-fructose, whilst the more soluble, rhombic leaflets, m. p. 162—163°, D^{17} 1·634, osazone m. p. 169—170° (decomp.), was *dl*-sorbose, the identity being confirmed by comparison with an artificial mixture of the enantiomorphous forms. The *dl*-fructose, here obtained crystalline for the first time, of course represents α-acrose, whilst the *dl*-sorbose in spite of the somewhat higher m. p. doubtless represents the β-acrose which had previously not been obtained in a quite pure condition. The formation of a racemic sorbose would be expected on theoretical grounds from the condensation of dihydroxyacetone with *dl*-glyceraldehyde.   D. F. T.

Cyanohydrins of Certain Monosaccharides. CYRILL KRAUZ and JAN KLOUD (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 397—401).—On the addition of hydrogen cyanide to a monosaccharide, two epimeric cyanohydrins are produced :

$$\cdot -CH(OH)\cdot CHO + HCN = CN\cdot CH(OH)\cdot CH(OH)-$$
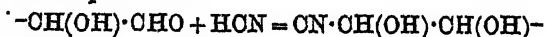
(compare Votoček, A., 1911, i, 179). A study has now been made of

the products obtained by the action of hydrogen cyanide on certain monosaccharides.

When arabinose is treated with solution of hydrogen cyanide, a mixture of the amides of l-gluconic and l-mannonic acids is obtained; the former has m. p. 181°, not 160° (decomp.) as stated by Kiliani (A., 1887, 230). In the case of xylose and rhamnose, liquid products were obtained which could not be separated. Rhodeose yields α- and β-rhodeohexonamides (Krauz, A., 1910, i, 224). Fucose furnishes α-fucohexonamide and β-*fucohexonamide*, m. p. 176°. With galactose, α-galactoheptonamide, m. p. 201°, was obtained; the mother liquor when treated with phenylhydrazine gave the phenylhydrazide of this amide, m. p. 226°, together with another phenylhydrazide, m. p. 186°. Mannose yields a mixture of α- and β-mannoheptonamides, the former melting at 214—215°, and not at 182—183° (Fischer and Hirschberger, A., 1889, 482).   E. G.

Hydrolysis of Cellulose. I. RICHARD WILLSTÄTTER and LÁSZLÓ ZECHMEISTER (*Ber.*, 1913, **46**, 2401—2412). —Whereas ordinary concentrated hydrochloric acid (37·6% of hydrogen chloride) decomposes and gelatinises cellulose after about a day's action, a more concentrated acid (40—41% of hydrogen chloride) dissolves cellulose completely within a few seconds. At first the cellulose can be precipitated again, but it is rapidly hydrolysed, and finally only dextrose remains in solution. It is possible to follow the course of the change both polarimetrically and gravimetrically, whereby 96% of the theoretical quantity of dextrose is obtained. The 1% solution of cellulose in the concentrated acid is at first optically inactive; it becomes active after about an hour, and increases until hydrolysis is complete in twenty-four to forty-eight hours at the ordinary temperature. The change in rotatory power gives indication of the intermediate formation of higher carbohydrates. An acid, D^{15} 1·212 (41·4% of hydrogen chloride), dissolves 15% of cellulose; the solution is at first colourless and clear; in time it becomes yellow, and later dark yellow as the dextrose is decomposed. On dilution of the solution during the first half-hour, unchanged cellulose is precipitated.

Cellulose dissolves similarly in 66% (D 1·78) hydrogen bromide, but not in concentrated hydriodic acid; hydrofluoric acid (70—75% of hydrogen fluoride) gelatinises, and quickly dissolves cellulose.

Pine-wood dissolves quickly in fuming hydrochloric acid, leaving 30% of its weight undissolved as lignin substance.

The rotatory power of dextrose ($[\alpha]_D$) increases from $+54·5°$ in hydrochloric acid D 1·018 to $+97·5°$ in an acid D 1·204, $+106°$ in an acid D 1·212, and $+164·6°$ in a 44·5% acid.   E. F. A.

Certain Substances containing the Cetyl Radicle. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1913, **27**, 217—225).—Triethylcetylammonium iodide, $C_{16}H_{33}\cdot NEt_3I$, is obtained when a mixture of triethylamine and cetyl iodide is heated for two hours at 130°. It dissolves in water, yielding soapy solutions, which develop an abundant

lather when shaken. These solutions only give an opalescence with silver nitrate, and thus appear to be colloidal, this observation being confirmed by a study of their b. p.'s and electrical conductivities. The solid iodide has m. p. 179—181° without decomposition (contrast Krafft and Moye, A., 1889, 689).

An attempt has been made to prepare triethylcetylammonium hydroxide by the action of freshly prepared silver oxide on a boiling alcoholic solution of the corresponding iodide. Under these conditions, however, the base, if formed, is decomposed into diethylcetylamine.

Aqueous solutions of diethylcetylamine hydrochloride behave similarly to those of the above iodide. Determinations of the conductivity at different temperatures show that a period of rapid crystallisation occurs in the region of 0°. The values obtained for the molecular conductivity are greater than those observed for triethylcetylammonium iodide at similar dilutions.

Triethylcetylammonium cetylsulphonate, $C_{16}H_{33} \cdot SO_3 \cdot NEt_3 \cdot C_{16}H_{33}$, is readily prepared by heating a boiling alcoholic solution of *silver cetylsulphonate* with triethylcetylammonium iodide. It is molten at 172—179° without showing any distinct m. p. It yields soapy solutions in hot water, which, on cooling, separate into a clear liquid and a jelly-like mass. It is soluble in alcohol and in ethyl acetate. From the latter it separates in crystals, m. p. about 53°, which contain solvent of crystallisation. Determinations of the conductivity of aqueous solutions lead to the conclusion that the substance is probably present in the form of multi-molecular aggregates.

In chemical constitution and in the behaviour of their aqueous solutions or pseudo-solutions, these substances are somewhat analogous to soaps. This is confirmed by the fact that solutions of triethylcetylammonium iodide or, better, of diethylcetylamine hydrochloride in water yield excellent results in the cleansing of samples of wool.

<div align="right">H. W.</div>

The Homologue of Muscarine in the C_3 Series   V. Brabant (*Zeitsch. physiol. Chem.*, 1913, **86**, 206—214).—To prepare β homo-muscarine acraldehyde is converted into ethyl αγ-dichloropropyl ether, $CH_2Cl \cdot CH_2 \cdot CHCl \cdot OEt$, and this into the ethylacetal of β-chloropropaldehyde, $CH_2Cl \cdot CH_2 \cdot CH(OEt)_2$. When this is heated with trimethylamine in a sealed tube on the water-bath, the *hydrochloride* of β homo-*muscarineacetal*, $NMe_3Cl \cdot CH_2 \cdot CH_2 \cdot CH(OEt)_2$, is obtained.

This is hydrolysed by concentrated hydrochloric acid to β-homo-*muscarine hydrochloride*, $NMe_3Cl \cdot CH_2 \cdot CH_2 \cdot CHO$, which shows all the typical reactions of both aldehyde and amino-groups.

β-Homomuscarineacetal hydrochloride forms stellate aggregates of small needles which are very hygroscopic; the *platinichloride* forms large, prismatic-rhombic, orange-red crystals which blacken at 160°, m. p. 190—195° (decomp.); the *aurichloride* separates in broad, lustrous, straw-yellow needles, m. p. 93—95° (decomp.).

β-Homomuscarine hydrochloride forms hygroscopic crystals; the free base could not be isolated. The *platinichloride* separates in microscopic, orange-yellow rods, decomp. 156—160°. The *auri-*

chloride is straw-yellow, m. p. 150—155° (decomp.). The *semicarbazone* crystallises in small, colourless, regular octahedra, m. p. 247 5° (corr.).

E. F. A.

Compounds of Hydrated Salts with Organic Bases (Dithionates, Sulphates, Thiosulphates). FILIPPO CALZOLARI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 787—792. Compare A , 1912, i, 812).— The dithionate, $MgS_2O_6,8H_2O,2C_8H_{10}O_2N_4$, prepared from magnesium dithionate and a large excess of caffeine, forms colourless, prismatic crystals. The *manganese* derivative, $MnS_2O_6,8H_2O,2C_8H_{10}O_2N_4$, crystallises in colourless needles. The *ferrous* salt,

$$FeS_2O_6,8H_2O,2C_8H_{10}O_2N_4,$$
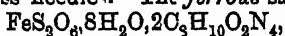
forms prismatic crystals. The *cobalt* salt, $CoS_2O_6,8H_2O,2C_8H_{10}O_2N_4$, crystallises in pale rose-coloured needles. The *nickel* salt,

$$NiS_2O_6,8H_2O,2C_8H_{10}O_2N_4,$$
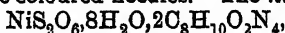
forms green crystals isomorphous with those of the cobalt compound.

The compound of magnesium dithionate with hexamethylenetetramine, $MgS_2O_6,6H_2O,2C_6H_{12}N_4$, forms large crystals. The *manganese* compound, $MnS_2O_6,6H_2O,2C_6H_{12}N_4$, is a white, crystalline powder. The *ferrous* salt, $FeS_2O_6,6H_2O,2C_6H_{12}N_4$, is a greenish-white, crystalline powder. The *cobalt* salt, $CoS_2O_6,6H_2O,2C_6H_{12}N_4$, forms rose-red, regular crystals. The *nickel* salt, $NiS_2O_6,6H_2O,2C_6H_{12}N_4$, forms green crystals similar to those of the cobalt compound.

The *compound* of magnesium sulphate and hexamethylenetetramine, $MgSO_4,9H_2O,C_6H_{12}N_4$, forms colourless crystals. The *manganese* compound, $MnSO_4,9H_2O,C_6H_{12}N_4$, forms colourless crystals, and mixed crystals of this compound with that of nickel were also obtained. The *ferrous* compound, $FeSO_4,9H_2O,C_6H_{12}N_4$, must be prepared in the absence of air. The *cobalt* compound, $CoSO_4,9H_2O,C_6H_{12}N_4$, forms rose-red crystals, and mixed crystals of it with the magnesium compound can be obtained. The *nickel* compound, $NiSO_4,9H_2O,C_6H_{12}N_4$, forms large, emerald-green crystals isomorphous with those of the cobalt salt.

The compound of magnesium thiosulphate with hexamethylenetetramine, $MgS_2O_3,8H_2O,C_6H_{12}N_4$, forms colourless, rhombohedral crystals. The *manganese* compound, $MnS_2O_3,8H_2O,C_6H_{12}N_4$, forms very pale rose-coloured crystals. The *ferrous* compound,

$$FeS_2O_3,8H_2O,C_6H_{12}N_4,$$
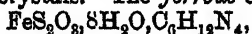
must be prepared out of contact with the air; it forms greenish-white crystals. The *cobalt* salt, $CoS_2O_3,8H_2O,C_6H_{12}N_4$, forms rose-coloured crystals. The *nickel* compound, $NiS_2O_3,8H_2O,C_6H_{12}N_4$, forms emerald-green crystals.

R. V. S.

Condensation of Amino-acids with Formaldehyde. GINO GALEOTTI (*Biochem. Zeitsch*, 1913, 53, 474—492).—On heating aminoacids with formaldehyde, products are obtained which differ both from the original acids and fresh mixtures of the reacting products. Reddish-yellow solutions are obtained, which do not deposit crystals, but yield an amorphous residue on evaporating off the water. The solutions are acid, and only the tyrosine derivative is precipitated on the addition of dilute acids. The glycine, alanine, aspartic acid

and tyrosine derivatives are insoluble in alcohol or acetone, but the leucine and phenylalanine derivatives are soluble. All are insoluble in ether. The aqueous solutions give voluminous precipitates with phosphotungstic, picric and tannic acids, and with the salts of heavy metals. They do not reduce copper salts in alkaline solution, give the diazo-reaction with a yellowish-red or cherry-red colour, and give precipitates on saturation with ammonium sulphate. They dissolve copper hydroxide, yielding malachite-green solutions which give a precipitate on addition of alcohol. They no longer contain the amino-group, as no nitrogen is evolved in the van Slyke reaction, which can be employed for tracing the course of the reaction of the aldehyde on the acids. The glycine derivative was studied in some detail. It has a molecular weight of 288, corresponding with the formula $C_{12}H_{21}O_5N_3$, and m. p. 164°. Attention is called to the similarity in the behaviour of the compounds obtained to the polypeptides, and it is suggested that formaldehyde may play some part in forming complex derivatives from amino-acids in living organisms, analogous to the supposed formation of carbohydrates by condensation with this substance.   S. B. S.

Synthesis of the Anhydrides of α-Aminoacyl Glucosamines. CHARLES WEIZMANN and ARTHUR HOPWOOD (*Proc. Roy. Soc.*, 1913, *A*, 88, 455—461. Compare P., 1912, 28, 261).—α-Bromoacyl haloids are condensed with glucosamine hydrochloride in the presence of sodium hydroxide (compare P., 1912, 28, 261), and cold aqueous ammonia is allowed to act on the α-bromoacylglucosamines formed. Anhydrides of the expected α-aminoacylglucosamines are obtained.

Alanylglucosamine anhydride separates in colourless, prismatic needles, which turn brown at 245—250°, and melt at 269—272° to a black liquid. It reduces Fehling's solution on prolonged boiling, but does not react with either phenylhydrazine or semicarbazide.

Leucylglucosamine anhydride forms similar colourless, prismatic needles, which sinters at 205°, m. p. 213—215° (decomp.).

α-Aminolaurylglucosamine anhydride was obtained in colourless crystals.   •   E. F. A.

Esters of Imino- and Oximino-carbonic Acid. JOSEPH HOUBEN and ERICH SCHMIDT (*Ber.*, 1913, 46, 2447—2460).—Sandmeyer (A., 1886, 611) claimed to have reduced esters of chloroiminocarbonic acid, and obtained ethyl iminocarbonate, $HN{:}C(OEt)_2$, which was dried over potassium hydroxide. It is shown that under these conditions urethane is formed, and that it was present in Sandmeyer's product.

When the reduction product is carefully dried over ignited sodium sulphate and fractionated in a vacuum, pure iminocarbonic esters are obtainable. Even the pure esters change on prolonged keeping into crystalline cyanuric acid derivatives.

The hydrochloride of the imino-ester is to be regarded as a chloroimino-ether, $NH_2 \cdot CCl(OR)_2$. In presence of water the chlorine is exchanged for hydroxyl, $NH_2 \cdot C(OR)_2 \cdot OH, HCl$, following which the hydrogen chloride conditions elimination of ammonium chloride and the formation of alkyl carbonate, $CO(OR)_2$.

Similarly, with hydroxylamine the compound

$$NH_2 \cdot C(OR)_2 \cdot NH \cdot OH, HCl$$
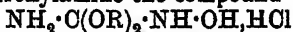
formed decomposes into the oximinocarbonic ester, $C(OR)_2:N \cdot OH$. Working in ethereal solution it was possible to prepare *diethyl* or *dimethyl oximinocarbonate* in this manner, and the method has been extended to the preparation of the true hydroximic esters of the aliphatic series, $OEt \cdot CR:N \cdot OH$.

The oximinocarbonic esters, which crystallise well, are obtained by a similar process from the chloroiminocarbonic esters.

Ethyl chloroiminocarbonate has m. p. 39°, agreeing with Sandmeyer's statement; during its preparation a product of unknown constitution crystallising in needles, m. p. 148—149°, is formed.

Methyl chloroiminocarbonate has m. p. 20°, b. p. 63—64°/13 mm., without decomposition.

Ethyl iminocarbonate is a transparent liquid of a strongly basic odour, D^{22} 0·9637.

Ethyl iodoiminocarbonate, $NI:C(OEt)_2$, forms yellow crystals and crusts. When shaken with mercury in ethereal or alcoholic solution, *aziethyl carbonate*, $C(OEt)_2:N \cdot N:C(OEt)_2$, is formed.

Ethyl carbanilinoiminocarbonate, $C_6H_5 \cdot NH \cdot CO \cdot N:C(OEt)_2$, forms crystals sintering at 100°, m. p. 101°.

Ethyl thiocarbanilinoiminocarbonate has m. p. 117—118°.

E. F. A.

The Organic Acid Amides and their Metallic Derivatives as Acids and Salts of the Ammonia System of Acids, Bases, and Salts. EDWARD C. FRANKLIN (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 119—130. Compare A., 1912, ii, 451).—A recapitulation of the author's classification of amides and their derivatives into "ammonoacids," "ammono-bases," "ammono salts," "ammono-esters," "mixed ammono-acids," and "acid anammonides." The ammono-acids vary in strength from acetamide, benzamide, and carbamide, which only form salts in liquid ammonia solution and have only a feeble conductivity in that solvent, to such compounds as phthalimide and "saccharin" which are not excelled in strength by the strongest carboxylic acids.

J. C. W.

Compounds of Ferricarbamide. GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 867—870).—These compounds exhibit complete chemical and crystallographic similarity to the salts of chromicarbamide already known. They are all greenish-blue in the solid state and in concentrated solution, but dilute solutions are yellow and are precipitated by ammonia even in the cold. Compounds analogous to the hydrate and carbonate of chromicarbamide cannot be prepared.

The *perchlorate*, $[Fe(CON_2H_4)_6](ClO_4)_3$, is obtained by adding a concentrated solution of carbamide to a solution of ferric perchlorate containing excess of perchloric acid, or from a perchlorate and another ferricarbamide compound. It forms mixed crystals with the corresponding *chromicarbamide perchlorate*, $[Cr(CON_2H_4)_6](ClO_4)_3$, which is a green, crystalline powder.

Ferricarbamide nitrate, $[Fe(CON_2H_4)_6](NO_3)_3$, the *permanganate,* $[Fe(CON_2H_4)_6](MnO_4)_3$, the *dichromate,* $[Fe(CON_2H_4)_6](Cr_2O_7)_3$, the *chloride,* $[Fe(CON_2H_4)_6]Cl_3,3H_2O$, the *bromide,*
$$[Fe(CON_2H_4)_6]Br_3,3H_2O,$$
and the *nitrate periodide,* $[Fe(CON_2H_4)_6](NO_3)_2I,I_2$, are similarly prepared. On treating the bromide with bromine an unstable perbromide is obtained.   R. V. S.

Preparation of Melamine and Ammeline from Dicyanodiamide ; Triaminomelamine and Diaminoammeline. ROBERT STOLLÉ and K. KRAUCH (*Ber.*, 1913, **46**, 2337—2339).—When powdered dicyanodiamide is treated with concentrated ammonia solution in a sealed tube at 120° for three hours, a crystalline deposit is obtained consisting of melamine in 35% yield and of ammeline in 20% yield, which can be separated by the sparing solubility of the latter in water ; a small quantity of carbamide and guanidine can be found in the liquid from which the crystalline mass has separated. It is suggested that possibly the dicyanodiamide is acted on concurrently by the ammonia and by water, with the production of guanidine and cyanamide and of guanidine and cyanic acid respectively ; unchanged dicyanodiamide then reacts with the cyanamide yielding melamine, and with the cyanic acid yielding ammeline.

Triaminomelamine (cyanuric hydrazide ; von Meyer and Näbe, A., 1911, i, 122 ; Finger, A., 1907, i, 298), microscopic needles, m. p. 287°, was obtained by heating melamine with a quinquemolecular proportion of hydrazine hydrate for five hours under pressure at 150° ; it quickly reduces warm ammoniacal silver nitrate, and when shaken in hydrochloric acid solution with benzaldehyde yields a *tribenzylidene* derivative.

When ammeline is heated with an equal quantity of hydrazine hydrate for five hours under pressure at 130°, diaminoammeline, prisms, m. p. above 340°, is obtained ; this in aqueous solution reacts with benzaldehyde, producing a *dibenzylidene* derivative, m. p. 315°.
                                        D. F. T.

Condensation of Melamine with Dextrose. LEOPOLD RADLBERGER (*Chem. Zentr.*, 1913, i, 2110 ; from *Öster-ung Zeitsch. Zuckerind.*, 1913, **42**, 236—239).—Melamine and dextrose were condensed by heating in 30% alcoholic solution on the water-bath. The product consisted of 2 mols. melamine to 1 mol. dextrose, namely, $[C_3N_3(NH_2)_2\cdot NH]_2CH\cdot[CH\cdot OH]_4\cdot CH_2\cdot OH$. It has m. p. 281°, forming colourless, lustrous crystals which do not reduce Fehling's solution.
                                        E. F. A.

Synthesis of Mercury Fulminate from Propyl Alcohol. A. L. KIBLER (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 239—243). —Experiments are described in which propyl alcohol, *iso*butyl alcohol, amyl alcohol, acetone, and propaldehyde were substituted for ethyl alcohol in the usual process for the preparation of mercury fulminate. A small quantity of mercury fulminate was obtained from the propyl alcohol, but not from any of the other substances. In the experi-

ments with propyl alcohol, an intermediate compound was isolated, which forms large, white, lustrous plates, and decomposes either spontaneously or when treated with water, leaving traces of a grey powder, probably composed of mercury.　　　　　　　　　　E. G.

Azides of Carbamic Acid from Ketens. VII. E. OLIVERI-MANDALÀ and E CALDERARO (*Gazzetta*, 1913, **43**, i, 538—543. Compare this vol., i, 716).—Azoimide reacts with ketens giving azides of carbamic acid. The stages in the reaction are probably indicated by the scheme: $CR_2 \text{:} CO \longrightarrow CHR_2 \cdot CO \cdot N_3 \longrightarrow [CHR_2 \cdot CO \cdot N] \longrightarrow CHR_2 \cdot N \text{:} CO$, and from this carbimide the azide, $CHR_2 \cdot NH \cdot CO \cdot N_3$, is produced by the addition of a further molecule of azoimide.

Keten reacts with an ethereal solution of azoimide at the temperature of a mixture of ice and salt, yielding *methylcarbamazide*, $N_3 \cdot CO \cdot NHMe$, which forms lustrous laminæ or tablets, m. p. 46—47°. The formation of the azide shows that keten has reacted as though it had the ketonic formula of Staudinger, and not the hydroxylic formula of Wilsmore. With aniline, the azide yields *s*-phenylmethylcarbamide and aniline azoimide. Alcoholic ammonia reacts with the azide, yielding methylcarbamide and ammonium azoimide. Boiling water decomposes the azide, carbon dioxide, azoimide and methylamine being formed; by keeping an aqueous solution of the azide in a desiccator, *methylammonium azoimide*, CH_5N_4, can be obtained; it is a deliquescent substance, which is completely fused at 115°.

Diphenylketen and azoimide yield *diphenylmethylcarbamazide*,
$$N_3 \cdot CO \cdot NH \cdot CHPh_2,$$
which crystallises in colourless, silky needles, m. p. 121—123°. When heated for four hours at 100—110° in a sealed tube with alcoholic ammonia, the azoimide yields *as*-diphenylmethylcarbamide. When heated with aniline in a sealed tube for two hours at 90°, the azide is converted into *diphenylmethylphenylcarbamide*,
$$NHPh \cdot CO \cdot NH \cdot CHPh_2,$$
which forms silky crystals, m. p. 208—209°. This substance dissolves in concentrated sulphuric acid, giving an orange-red coloration.　　　　R. V. S.

Action of Magnesium Methyl Iodide on Silicon Hexachloride. GEOFFREY MARTIN (*Ber.*, 1913, **46**, 2442—2447. Compare P., 1913, **29**, 190).—The yellow substance formed by the action of magnesium methyl iodide on silicon hexachloride has the composition $Si_6H_9O_{13}Me$. When heated, hydrogen and methane are evolved, and a silicon compound is obtained practically without carbon, but which still contains coupled silicon groups, since on dissolution in potassium hydroxide hydrogen is evolved. On the addition of excess of acid, silicic acid is precipitated.　　　　　　　　　　E. F. A.

Researches on the Direct Introduction of Substituents into the Benzene Nucleus During the Years 1910, 1911, and 1912. ARNOLD F. HOLLEMAN (*Chem. Weekblad*, 1913, **10**, 604—620). —A summary of papers on this subject published since the issue of

the author's work, "Die direkte Einfuhrung von Substituenten in den Benzolkern," in the year 1910. A. J. W.

A Simple Method of Preparing Hexamethylbenzene. HANS RECKLEBEN and JOHANNES SCHEIBER [with K. SCHNABEL] (*Ber.*, 1913, 46, 2363—2365).—When the vapour from a molecular mixture of acetone and methyl alcohol is passed over aluminium oxide, heated at about 400°, clean crystals of hexamethylbenzene are obtained in about 10% of the theoretical quantity. The oily residue represents a complicated mixture. Replacement of aluminium oxide by other oxides led to unfavourable results.

On bromination of hexamethylbenzene, a mixture of bromides, m. p. 231—269°, and containing from 64% to 80% of bromine, is obtained. E F. A.

Nitro-derivatives of High-boiling Mineral Oils. KONSTANTIN CHARITSCHKOFF (*Chem. Zeit.*, 1913, 37, 869).—When Caucasian lubricating oils are warmed with fuming nitric acid, they form syrupy, very viscous nitro-derivatives, which are soluble in most organic solvents with the exception of light petroleum. They are weak acids, dissolve in alkalis, and form insoluble salts with the alkaline earths and heavy metals which are similar to the salts of polynaphthenic acids (A., 1910, i, 110). Moreover, their composition and properties agree with those of the nitro-derivatives of polynaphthenic acids.

J. C. W.

The Reaction Between Selenic Acid and Toluene. HOWARD WATERS DOUGHTY and FRANK ROSE ELDER (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 93—101).—Toluene and concentrated selenic acid were left together for some months during which time carbon dioxide was evolved. The lower, dark red, viscous layer was then poured into water and separated into an acid solution and a small amount of a red oil with a solid admixture.

The acid solution was exactly neutralised with barium hydroxide, filtered from barium selenate, evaporated to dryness, and extracted during several days with chloroform, which removed traces of the above red oil. The residue gave a mixture of *o*- and *p*-tolueneselenonic acids which could not be separated, but on reduction of a concentrated solution with hydrogen chloride, p(?)-*tolueneseleninic acid*, $C_6H_4Me \cdot SeO_2H, H_2O$, was precipitated in long, silky, white needles, m. p. 160°, whilst the mother liquor yielded o(?) *tolueneseleninic acid*, with $\frac{1}{2}H_2O$, in nodules of short, white needles, m. p. 99—101°.

The red oil was washed with ether in which the solid substance is insoluble, and then distilled. It had b. p. 201—202°/18—20 mm., and solidified to a light yellow, crystalline mass, m. p. 69·5—70·5°, which was identified with *p*-ditolyl selenide (Zeiser, A., 1895, i, 512). On oxidation with hot permanganate, it yielded *diphenylselenone*-4 : 4'-*dicarboxylic acid*, $SeO_2(C_6H_4 \cdot CO_2H)_2$, as a heavy, white solid, m. p. 283°, which is sparingly soluble in hot alcohol, and insoluble in all other common solvents.

The crystalline substance, insoluble in ether or water, was recrystal-

lised from alcohol in colourless, stout, hexagonal prisms, m. p. 183°. It was not affected by boiling alkalis or permanganate, but yielded salicylic acid on fusion with potassium hydroxide. It is, therefore, *benzophenoneselenone* (III), and its formation is explained by assuming that *o*-ditolyl selenide (I) is formed as an intermediate product, and is then oxidised to diphenylselenone-2 : 2'-dicarboxylic acid (II), which condenses with loss of carbon dioxide and water.
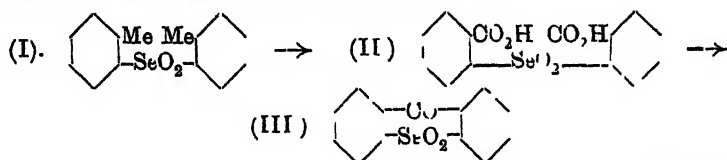
<div style="text-align:right">J. C. W.</div>

Action of Sodium in Liquid Ammonia on Phenylacetylene and Styrene. PAUL LEBEAU and MARIUS PICON (*Compt. rend.*, 1913, 157, 223—224. Compare this vol., i, 950).—Sodium in liquid ammonia reacts with phenylacetylene, giving the corresponding sodium derivative (2 mols.) and ethylbenzene (1 mol), with the formation of sodamide. Unlike the true acetylenes of the fatty series, the hydrogenation does not stop at the ethylenic hydrocarbon, but the fully saturated hydrocarbon is produced :

$$3CPh\ddot{:}CH + 4NH_3Na = 2CPh\ddot{:}ONa + C_6H_5 \cdot Et + 2NaNH_2 + 2NH_3.$$

Styrene itself reacts slowly with sodium in liquid ammonia, the products being ethylbenzene and sodamide. W. G.

A Yellow Hydrocarbon of the Fluorene Series. RUDOLF PUMMERER and GUSTAV DORFMÜLLER (*Ber.*, 1913, 46, 2386—2389).— When fluorene is heated with lead dioxide and sodium ethoxide in pyridine solution, small quantities of a yellow hydrocarbon are formed, owing to the formation of acetaldehyde, and coupling of this with two molecules of fluorene. The final product is *dehydroethylidenebisfluorene* (I), but *ethylidenebisfluorene* (II) is formed first, and may also be obtained by reducing the dehydro-compound with zinc dust and acetic acid. It is very readily oxidised by lead dioxide and even by atmospheric oxygen. The double bond only very slowly absorbs bromine, and does not react with permanganate in pyridine solution.
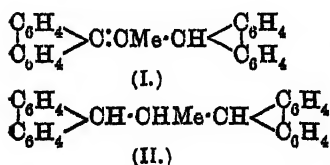
Dehydroethylidenebisfluorene crystallises in oblique-ended, yellow prisms ; it darkens at 280°, but has not melted at 350°. In small quantities it apparently distils unchanged.

Ethylidenebisfluorene is colourless, m. p. 262—263°, to a yellowish-brown liquid. E. F. A.

Orthohalogenated *p*-Nitroanilines and their Derivatives. WILHELM KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 823—836).—2-Chloro-4-nitroaniline forms pale yellow

needles, m. p. 104·5°. Its acetyl derivative crystallises in straw-coloured prisms, m. p. 139°.

3-*Chloro-4-bromo-1-nitrobenzene* (obtained from the perbromide of the diazonium compound of the preceding substance) forms colourless needles or prisms, m. p. 62°.

3-*Chloro-4-iodo-1-nitrobenzene* (similarly prepared) crystallises in almost colourless needles, m. p. 103°.

2-Bromo-4-nitroaniline crystallises in pale yellow needles, m. p. 104·5°. Its monoacetyl derivative forms flat prisms, m. p. 114°; the *diacetyl* derivative in stout prisms, m. p. 132°.

From the amino-derivative by diazotisation, 4-chloro-3-bromo-1-nitrobenzene can be obtained; it crystallises in almost colourless prisms, m. p. 61°. and is identical with the compound obtained from 6-chloro-3-nitroaniline. The corresponding 3-bromo-4-iodo-1-nitrobenzene crystallises in needles or prisms, m. p. 106°. 2-Iodo-4-nitroaniline, m. p. 109°, occurs in yellowish-red prisms and also in golden-yellow laminæ; the former is the more stable form. The substance yields a *monoacetyl* and a *diacetyl* derivative.

2-Iodo-4-nitroaniline can be diazotised, and by the subsequent introduction of chlorine, 4-chloro-3-iodo-1-nitrobenzene can be prepared; it crystallises in colourless needles, m. p. 78°, and is identical with the compound obtained from 6-chloro-3-nitroaniline in a similar way.

2 : 6-Dichloro-4-nitroaniline crystallises in lemon-yellow needles, m. p. 195°. It is best diazotised in nitric acid (D 1·38) at 0°. It yields a monoacetyl derivative (almost colourless, flat needles, m. p. 215°) and a diacetyl derivative, m. p. 142·5°, which crystallises in prisms of the monoclinic system

[E. Artini: $a : b : c = 1·1361 : 1 : 0·8753$; $\beta = 70·4°$, D 1·565].

When an alcoholic solution of the preceding amino-compound containing a little concentrated sulphuric acid is treated with ethyl nitrite, 3 : 5-dichloro-1-nitrobenzene is produced; it crystallises in colourless plates, m. p. 65·4°. On reduction with tin and hydrochloric acid it yields the corresponding dichloroaniline, which forms needles or prisms, m. p. 51·5°. From this substance, 1 : 3 : 5-trichlorobenzene is obtainable; it crystallises in colourless needles, m. p. 63·5°, and is identical with that obtained from 2 : 4 : 6-trichloroaniline, m. p. 77·5°. 3 : 5-Dichloro-1-bromobenzene crystallises in colourless needles, m. p. 75·8°. 3 : 5-*Dichloro-1-iodobenzene* has m. p. 54°; it is identical with that obtained from 2 : 4-dichloro-6-iodoaniline, m. p. 84°.

3 : 4 : 5-Trichloro-1-nitrobenzene (from 2 : 6-dichloro-4-nitroaniline) forms pale yellow prisms, m. p. 72·5°. On reduction and elimination of the amino-groups it yields 1 : 2 : 3-trichlorobenzene, m. p. 50·8°, identical with that obtained from 2 : 6-dichloroaniline (Körner and Contardi, A., 1909, i, 220).

3 : 5-Dichloro-4-bromo-1-nitrobenzene (from the dichloronitro-derivative) crystallises in pale yellow prisms, m. p. 88°.

3 : 5-*Dichloro-4-iodo-1-nitrobenzene* forms yellow prisms, m. p. 154·8°. On reduction with ferrous sulphate and ammonia, and subsequent elimination of the amino-group, it yields 1 : 3-*dichloro-2-iodobenzene*, which crystallises in thin, colourless plates, m. p. 68°. The same

substance can be prepared from the 2 : 6-dichloroaniline already mentioned.

2 : 6-Dibromo-4-nitroaniline (by the action of bromine on *p*-nitroaniline) crystallises in golden-yellow laminæ, m. p. 202·5°. Its monoacetyl derivative forms almost colourless needles, m. p. 232°. The diacetyl derivative, m. p. 136°, crystallises in the pinaconic class of the triclinic system [*a* : *b* : *c* = 1·0901 : 1 : 0·8325, α 88°43′4″, β 70°49′34″, γ 93°25′39″, D 1·939].

3 : 5-Dibromo-1-nitrobenzene is obtained by diazotising (in alcoholic solution containing sulphuric acid) either 2 : 6-dibromo-4-nitroaniline or 4 : 6-dibromo-2-nitroaniline ; it crystallises in thin, almost colourless laminæ, m. p. 104·5°. From it *s*-chlorodibromobenzene (m. p. 119°) and *s-dibromoiodobenzene* (m. p. 124·8°) can be readily prepared. These substances can also be obtained from the following corresponding halogenated anilines : 4-chloro-2 : 6-dibromoaniline (m. p. 102°) ; 2 : 6-*dibromo-4-iodoaniline* (colourless needles, m. p. 147°) ; 2 : 4-*dibromo-6-iodoaniline* (colourless needles, m. p. 123·5°).

3 : 4 : 5-Tribromo-1-nitrobenzene (from the perbromide of the diazocompound of the dibromonitroaniline already mentioned) crystallises in yellow prisms, m. p. 111·9°. On diazotisation and elimination of the amino-group it yields 1 : 2 : 3-tribromobenzene, m. p. 87·8°.

4-*Chloro*-3 : 5-*dibromo-1-nitrobenzene* (obtained in an analogous manner to the nitrotribromo-derivative) crystallises in yellow, tabular prisms, m. p. 92·7°. On reduction and elimination of the amino-group it yields 1-chloro-2 : 6-dibromobenzene, which forms colourless plates, m. p. 71°, and is identical with the product obtained from the corresponding dibromoaniline.

3 : 5-*Dibromo-4-iodo-1-nitrobenzene* crystallises in prisms, m. p. 135·5°. It is not possible to reduce this compound without altering it. The corresponding 1 : 3-dibromo-2-iodobenzene (colourless, tabular prisms, m. p. 72°) is prepared from *o*-dibromoaniline.

2 : 6-Di-iodo-4-nitroaniline (from iodine chloride and an acetic acid solution of *p*-nitroaniline) forms golden-yellow scales or flat needles, m. p. 245°. Its *monoacetyl* derivative forms slightly yellow needles, m. p. 249° ; the *diacetyl* derivative forms stout prisms, m. p. 171°, of the pinacoidal class of the triclinic system [*a* : *b* : *c* = 0·9682 : 0 : 0·7260, α 83°6′43″, β 76°8′29″, γ 99°42′44″, D 2·290].

3 : 5-Di-iodo-1-nitrobenzene (from the di-iodonitroaniline above described by diazotisation in alcoholic solution in presence of sulphuric acid) forms slightly yellow prisms, m. p. 104·5°. When reduced with ferrous sulphate and ammonia it gives 3 : 5-di-iodoaniline (colourless needles, m. p. 110°).

5-*Chloro*-1 : 3-*di-iodobenzene* is obtained from 4-chloro-2 : 6-di-iodoaniline, and forms lustrous, colourless needles, m. p. 101°.

5-*Bromo*-1 : 3-*di-iodobenzene* (similarly obtained) crystallises in long needles, m. p. 140°.

1 : 3 : 5-Tri-iodobenzene (from 2 : 4 : 6-tri-iodoaniline, m. p. 185·6°, or from *s*-di-iodoaniline, m. p. 110°) forms opaque, colourless needles, m. p. 184·2°.

4-*Chloro*-3:5-*di-iodo-1-nitrobenzene* (prepared by the action of cuprous chloride on the nitrate of the diazo-compound from 4 : 6-di-iodo-2-nitro-

aniline) crystallises in almost colourless needles, m. p. 110°. Reduction of this compound is best effected with an alcoholic solution of ammonium sulphide; a small quantity of a sulphur *compound* is formed at the same time. 2-*Chloro*-1 : 3-*di-iodobenzene* is obtained by decomposing the diazo-salt of this amino-compound with absolute alcohol; it forms thin, rhombic plates, m. p. 82°.

4-*Bromo*-3 : 5-*di-iodo*-1-*nitrobenzene* (from the nitrate of the diazo-compound of the di-iodonitroaniline and cuprous bromide) forms almost colourless needles, m. p. 125·4°, and crystallises from benzene with $1C_6H_6$ in prisms.

3 : 4 : 5-Tri-iodo-1-nitrobenzene (from di-iodonitroaniline by way of the diazo-compound) crystallises in shining yellow prisms. It is reduced (with difficulty) to the corresponding aniline by ferrous sulphate and ammonia, and when this is treated with an alcoholic solution of ethyl nitrite, 1 : 2 : 3-tri-iodobenzene (m. p. 116°) is obtained, identical with that from 2 : 6-di-iodoaniline (m. p. 122°; Körner and Bellasio, A., 1908, i, 778).

2-Chloro-6-bromo-4-nitroaniline is obtained by treating 2-chloro-4-nitroaniline with the calculated quantity of bromine; it forms yellow needles, m. p. 177·4°. The monoacetyl derivative crystallises in pale straw-coloured needles, m. p. 224°, and the diacetyl derivative, tabular prisms, m. p. 139° [prismatic class of the monoclinic system, $a : b : c = 1·1127 : 1 : 0·8509$, β 70·36°, D 1·749].

3-Chloro-5-bromo-1-nitrobenzene (from 2-chloro-6-bromo-4-nitroaniline by means of ethyl nitrite) crystallises in thin plates, m. p. 81·2°. On reduction with tin and hydrochloric acid it yields 3-*chloro*-5-*bromoaniline* (colourless needles or prisms), from which 1-*chloro*-5-*bromo*-3-*iodobenzene* can be prepared by way of the diazo-compound; it forms lustrous needles, m. p. 85·8°, and can also be obtained from 4-*chloro*-2-*bromo*-6-*iodoaniline*, which crystallises in needles, m. p. 110·5°.

3 : 4-*Dichloro*-5-*bromo*-1-*nitrobenzene* (from the corresponding chlorobromonitroaniline already described) forms yellow prisms, m. p. 82·4°.

5-*Chloro*-3 : 4-*dibromo*-1-*nitrobenzene* (similarly prepared) crystallises in yellow prisms, m. p. 99·5°. The corresponding 3-chloro-1 : 2-dibromobenzene (prepared by replacing $-NH_2$ by $-Br$ in 2-chloro-3-bromoaniline) forms rhombic plates, m. p. 72·6°.

3-*Chloro*-5-*bromo*-4-*iodo*-1-*nitrobenzene* (prepared in a similar way to its analogues above described) crystallises in lustrous needles, m. p. 159°.

2-Chloro-6-iodo-4-nitroaniline (from 2-chloro-4-nitroaniline and iodine chloride) forms pale yellow needles, m. p. 195°. Its *monoacetyl* derivative forms needles or prisms, m. p. 207°, and the *diacetyl* derivative, m. p. 113°, prisms of the monoclinic system [$a : b : c = 1·038 : 1 : 0·799$, $\beta = 71·44°$, D 1·913].

By elimination of the amino-group the preceding aniline yields 3-*chloro*-5-*iodo*-1-*nitrobenzene*, which forms bundles of prisms, m. p. 70·4°.

3 : 4-*Dichloro*-5-*iodo*-1-*nitrobenzene* (from the above-described aniline) crystallises in pale yellow prisms, m. p. 59°. It is not possible to obtain the corresponding aniline by reduction. Ammonia and ferrous sulphate reduce it very slowly, tin and hydrochloric acid yield

3-*chloro*-5-*iodoaniline* (colourless plates, m. p. 69·8°), whilst ammonium sulphide in alcoholic solution gives 3 : 4-dichloroaniline.

3-*Chloro*-4-*bromo*-5-*iodo*-1-*nitrobenzene* (prepared like the analogous compound above described) crystallises in almost colourless needles, m. p. 95°.

5-*Chloro*-3 : 4-*di*-*iodo*-1-*nitrobenzene* (from 2-chloro-6-iodo-4-nitroaniline) forms almost colourless needles, m. p. 146·5°.

2-*Bromo*-6-*iodo*-4-*nitroaniline* (from 2 - bromo - 4 - nitroaniline and iodine chloride) crystallises in pale yellow needles, m. p. 221°. The *monoacetyl* derivative forms yellow prisms, m. p. 226°, and the *diacetyl* derivative, m. p. 134°, stout prisms of the pinacoidal class of the triclinic system [$a : b : c = 0\ 9470 : 1 : 0·7288$, a 83°59′54″, β 77°30′18″, γ 99°6′14″, D 2·112].

3-*Bromo* 5-*iodo*-1-*nitrobenzene* (from the preceding aniline) forms thin, flat needles, m. p. 97·5°.

4-*Chloro* 3-*bromo*-5-*iodo*-1-*nitrobenzene* (from the above-described bromoiodonitroaniline) crystallises in yellow prisms, or in colourless needles, m. p. 84°.   R. V. S.

Preparation of Benzylamine. MARTIN O. FORSTER and HILDA M. JUDD (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 118).—A cheap laboratory process for the preparation of benzylamine hydrochloride is described. Benzyl chloride is occasionally shaken during three days with sodium azoimide in spirit, the benzylazoimide is extracted with ether, and, without purification, reduced by means of zinc dust and 50% acetic acid.   J. C. W.

Salts of Dibasic Organic Acids with *o*-, *m*-, **and** *p*-**Toluidine, and with** *m*-4-**Xylidine.** F. GRÜNWALD (*J. pr. Chem.*, 1913, [ii], **88**, 168—179).—The three toluidines and *m*-4-xylidine combine with malonic, succinic, malic, tartaric, and fumaric acids in aqueous solution to form acid salts. Attempts to prepare the normal salts were unsuccessful.

o-*Toluidine hydrogen malonate* crystallises in short prisms (decomp. 108°); the m-*toluidine* salt in colourless prisms (decomp. 93°). The corresponding *hydrogen succinates* also crystallise in prisms (decomp. 60° and 121° respectively).

o-*Toluidine hydrogen malate* forms leaflets (decomp. 120°); the isomeric m- and p-*toluidine* salts, colourless needles (decomp. 103° and 153°). *o*-*Toluidine hydrogen fumarate* crystallises in hexagonal leaflets (decomp. 150°); the m- and p-*toluidine* salts in colourless prisms (decomp. 165° and 175°).

Of the salts of *m*-4-xylidine, the *hydrogen malonate* forms thin needles (decomp. 93°), the *hydrogen succinate*, large prisms (decomp. 89°), the *hydrogen tartrate*, prisms (decomp. 170°), and the *hydrogen fumarate*, leaflets (decomp. 175°).

When heated with cupric oxide, an aqueous solution of *m*-toluidine hydrogen oxalate yields *cupric* m-*toluidine oxalate*, $Cu(C_9H_{10}O_4)_2$, which separates with $3H_2O$ in crystals resembling copper sulphate ; the acid oxalates of *o*- and *p*-toluidine do not form similar copper salts.

Cupric o-*toluidine malonate*, $Cu(C_{10}H_{12}O_4)_2, 5H_2O$, forms bluish-green

crystals, which become anhydrous and green at 100°. *Cupric* m-*tolui-dine malonate* separates with $3H_2O$ in steel-blue crystals; the anhydrous salt is green. *Cupric* p-*toluidine malonate* crystallises with $1H_2O$. *Cupric* m-4-*xylidine malonate*, $Cu(C_{11}H_{14}O_4)_2,3H_2O$, forms blue leaflets.

The acid toluidine succinates do not yield normal cupric salts.

When boiled with nickel hydroxide in aqueous solution, *o*-toluidine hydrogen malonate yields a *nickel* salt, which forms green crystals containing $6H_2O$; *nickel* m-*toluidine malonate*, $Ni(C_{10}H_{12}O_4)_2$, crystallises with $4H_2O$ in reddish-violet leaflets; *nickel* p-*toluidine malonate* forms green, rhombic leaflets containing $2H_2O$.

Nickel m-4-*xylidine malonate* separates in dove-grey crystals containing $4H_2O$.   F. B.

Interactions with Succinylglycyl Chloride and Hippuryl Chloride. JOHANNES SCHEIBER and HANS RECKLEBEN (*Ber.*, 1913, 46, 2412—2420).—*Succinylglycine*, $C_2H_4{<}{}^{CO}_{CO}{>}N \cdot CH_2 \cdot CO_2H$, is prepared by heating molecular proportions of succinic anhydride and glycine at 170—180°; the colourless crystals have m. p. 113°.

With phosphorus pentachloride, colourless needles, m. p. 76°, of *succinylglycyl chloride* are obtained.

The chloride reacts with aniline, forming *succinylglycylanilide*, which crystallises in colourless needles, m. p. 151°.

With benzene and aluminium chloride, *succinyliminoacetophenone*, $C_2H_4 \cdot (CO)_2 \cdot N \cdot CH_2 \cdot COPh$, is formed; it separates in colourless needles, m. p. 143—144°, and yields a colourless *phenylhydrazone*, m. p. 201°.

Condensation of succinylglycyl chloride with ethyl sodiomalonate in boiling ether gives *ethyl di(succinylglycyl)malonate*,

$$O[CO \cdot CH_2 \cdot N:(CO)_2 \cdot C_2H_4]_2(CO_2Et)_2;$$

it separates in colourless platelets, m. p. 107°, and gives no coloration with ferric chloride.

Phenylhydrazine converts it into *ethyl 1-phenyl-3-succinylimido-methyl-5-pyrazolone-4-carboxylate*,

$$C_2H_4:(CO)_2:N \cdot CH_2 \cdot C{<}{}^{CH(CO_2Et)}_{N\text{-----}NPh}{>}CO.$$
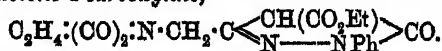
This crystallises in matted needles, m. p. 157°, giving a bluish-red coloration with ferric chloride.

Succinylglycylphenylhydrazide,

$$C_2H_4:(CO)_2:N \cdot CH_2 \cdot CO \cdot NH \cdot NHPh,$$

forms colourless needles, m. p. 213°.

A second product of the condensation is *ethyl succinylglycylmalonate*, $C_2H_4:(CO)_2:N \cdot CH_2 \cdot CO \cdot CH(CO_2Et)_2$, which forms colourless needles, m. p. 55°.

Succinylglycyl chloride and ethyl sodioacetoacetate condense to *ethyl succinylglycylacetoacetate*, of which the colourless needles have m. p. 102°.

Condensation with sodium acetylacetone leads to two products. *Succinylglycylacetylacetone*, $C_2H_4:(CO)_2:N \cdot CH_2 \cdot CO \cdot CH(COMe)_2$, forms

needles, m. p. 122°. *Di(succinylglycyl)acetylacetone* also yields needles, m. p. 150°.

Ethyl cyanosuccinylglycylacetate,

$$C_2H_4{:}(CO)_2{\cdot}N{\cdot}CH_2{\cdot}CO{\cdot}CH(CN){\cdot}CO_2Et,$$
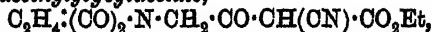
forms colourless needles, m. p. 73°.

Hippuryl chloride and ethyl sodiomalonate condense to a derivative of 2 : 5-*diketo*-1 : 4-*dibenzoylpiperazine* and *ethyl hippurylmalonate*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}CH(CO_2Et)_2$. The latter has m. p. 85°, and shows a positive ferric chloride reaction. With phenylhydrazine, *ethyl* 1-*phenyl*-3-*benzamidomethyl*-5-*pyrazolone*-4-*carboxylate,*

$$NHBz{\cdot}CH_2{\cdot}C{<}^{CH(CO_2Et)}_{N{-}\!\!-\!\!-NPh}{>}CO,$$

is obtained, m. p. 122—123°. It forms a well characterised, crystalline *sodium* salt. The above derivative of 2 : 5-diketo-1 : 4-dibenzoylpiperazine has m. p. 116°; it dissolves in sodium carbonate, and on precipitation with acid, a substance, m. p. 137°, is obtained containing $\frac{1}{2}H_2O$ less, and likewise giving a bluish-violet ferric chloride reaction ; on crystallising the compound m. p. 137° from ethyl alcohol, the substance of m. p. 116° is obtained. The latter is regarded as a condensation of two molecules of the piperazine with a molecule of water.

O-Hippurylacetylacetone, $NHBz{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CMe{:}CH{\cdot}COMe$, crystallises in platelets, m. p. 109°.

Ethyl cyanohippurylacetate, $NHBz{\cdot}CH_2{\cdot}CO{\cdot}CH(CN){\cdot}CO_2Et$, forms colourless needles, m. p. 139°. The additive product with phenylhydrazine has m. p. 107°. E. F. A.

Cholesterol. XVII. a-Cholestanol. ADOLF WINDAUS and C. UIBRIG (*Ber.*, 1913, 46, 2487—2491).—a-Cholestanol yields on oxidation a ketonic acid, $C_{32}H_{56}O_3$. This is not in agreement with the usual formula $C_{27}H_{48}O$ for cholestanol, and it is proved that the analytical data, particularly of cholestyl chloride and bromide, agree with the formula $C_{32}H_{56}O$ or $C_{32}H_{58}O$. Apparently on treatment of cholesterol with sodium and amyl alcohol, condensation and ring closure to a saturated compound takes place. Accordingly, cholestanol is not a dihydrocholesterol, but an *isoamyl* derivative of cholesterol,

$$C_{25}H_{44}{<}^{CH{\cdot}OH}_{CH{\cdot}C_5H_{11}}.$$
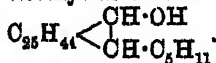
Cholestyl bromide crystallises in hexagonal platelets, m. p. 118°.

Ketocholestanolcarboxylic acid, $C_{25}H_{44}{<}^{CO_2H}_{CO{\cdot}C_5H_{11}}$, separates in long, slender needles which sinter at 110°, m. p. 125°. The *semicarbazone* crystallises in long needles, m. p. 207°. E. F. A.

Isomeric Naphthenic Acids. FRANK W. BUSHONG and I. W. HUMPHREY (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 57—67).—A quantity of commercial naphthenic acid from Baku, which contained about 50% of water and 5% of illuminating oils, was fractionally esterified. Several portions of 2 litres were heated with 200 c.c. of alcohol and 400 c.c. of sulphuric acid until the temperature rose to 140°, when a further 200 c.c. of alcohol was slowly run in. The distillate

was saponified, the hydrocarbons were removed by steam distillation, and, finally, the naphthenic acids were liberated and converted into methyl esters. These were fractionated and the constants of twenty-six fractions are given. The fraction 165—170° contained methyl hexanaphthenecarboxylate; fraction 189—192°, methyl heptanaphthene-carboxylate; fraction 210—212°, methyl octanaphthenecarboxylate, and fraction 220—224°, methyl nonanaphthenecarboxylate. The densities of the fractions rise continuously with the exception of fraction 200—204°, which agrees with the formula $C_8H_{15} \cdot CO_2Me$, and thus contains a methyl *iso*octanaphthenecarboxylate.

The residual, partly esterified naphthenic acids were then distilled in a current of natural gas from a copper still, when 40% passed over below 285° and 10% between 285—295°. The lower-boiling ethyl esters were redistilled and the fractions boiling below 236° were saponified, freed from hydrocarbons, and the naphthenic acids were finally separated into eighteen fractions. By means of diagrams it is shown that the optical-rotation curve for the acids is parallel to the curve for the methyl esters. The cause of the activity of petroleum is thus due to the naphthenic acids and not to impurities. The maximum lævorotation is exhibited by the hexanaphthenecarboxylic acid and its ester. J. C. W.

The Condensation of Aromatic Aldehydes with Pyruvic Acid. Eva Lubrzynska and Ida Smedley (*Biochem. J.*, 1913, 7, 375—379).—A full account of work of which an abstract has already appeared (P., 1913, 29, 174). W. D. H.

Camphenecarboxylic Acids and the Constitution of Camphene. Josef Houben and Ernst Willfroth (*Ber.*, 1913, 46, 2283—2299).—If Wagner's views with respect to the formation of camphene by the loss of hydrogen chloride from bornyl chloride are correct, the intermediate compound (II), formed by a similar removal of hydrogen chloride from α-chloro*allo*camphanecarboxylic acid (I), should give rise to two isomeric camphanecarboxylic acids (III and IV):

$$I. \quad \begin{array}{c} CH_2 \cdot CH - CH_2 \\ | \quad CMe_2 \quad | \\ CH_2 \quad | \quad CCl \cdot CO_2H \\ \diagdown CMe \diagup \end{array} \qquad II. \quad \begin{array}{c} CH_2 \cdot CH - CH_2 \\ | \quad CMe_2 \quad | \\ CH - \!\!\!-\!\!\!- C \cdot CO_2H \\ \diagdown CMe \diagup \end{array}$$

$$III. \quad \begin{array}{c} CH_2 \cdot CH - CH_2 \\ | \quad CMe_2 \quad | \\ CH_2 - \!\!\!\!\mid\!\!\!\!- C \cdot CO_2H \\ CH_2 : C \end{array} \qquad IV. \quad \begin{array}{c} CH_2 \cdot CH_2 - CH_2 \\ | \quad CMe_2 \quad | \\ CH - \!\!\!-\!\!\!- CH \cdot CO_2H \\ \diagdown C : CH_2 \end{array}$$
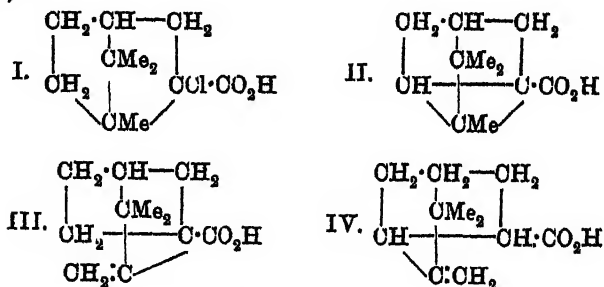
The authors find that two isomeric unsaturated acids of this composition are formed when the methyl ester of α-chloro*allo*camphane-carboxylic acid is heated with methyl-alcoholic potassium hydroxide, although only one of them could be isolated in a state of purity.

On oxidation, the camphanecarboxylic acids should be transformed into α- and β-camphenilonecarboxylic acids (V and VI).

$$\text{V.} \quad \begin{array}{c} \text{CH}_2\cdot\text{CH}\text{------}\text{CMe}_2 \\ | \qquad\qquad | \\ \text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{C(CO}_2\text{H)}\cdot\text{CO} \end{array} \qquad \text{VI.} \quad \begin{array}{c} \text{CH}_2\cdot\text{CH}\text{---}\text{CMe}_2 \\ | \qquad\qquad | \\ \text{CH}_2 \\ | \\ \text{CO}_2\text{H}\cdot\text{CH}\text{-}\text{CH}\text{---}\text{CO} \end{array}$$
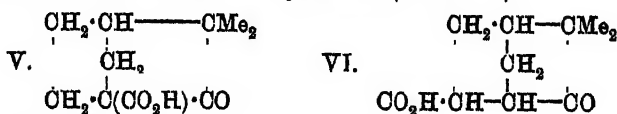
Oxidation of the acids formed by the removal of hydrogen chloride from chloro*allo*camphanecarboxylic acid resulted in the formation of two isomeric ketonic acids having the composition of the camphenilonecarboxylic acids. The investigation of these acids is not yet complete; both are very stable and can be distilled without decomposition, whereas α-camphenilonecarboxylic acid, being a β-ketonic acid, should be readily transformed by loss of carbon dioxide into camphenilone. In addition to the above ketonic acids, considerable quantities of hydropinenecarboxylic (*allo*camphanecarboxylic) acid were found amongst the oxidation products. It is probable that this acid was originally present in the mixture of unsaturated acids submitted to oxidation, and was formed by the reducing action of the methyl-alcoholic potassium hydroxide on the methyl ester of α-chloro*allo*camphanecarboxylic acid.

Hydropinenecarboxylic acid, prepared from pinene hydrochloride by Houber's method (A., 1906, i, 21), has m. p. 78°, $[\alpha]_D^{20} - 18\cdot26°$ in alcohol, and is converted by phosphorus pentachloride or thionyl chloride into the *chloride*, $C_{10}H_7\cdot COCl$, which forms a colourless liquid, b. p. 110°/10 mm., and yields a *methyl* ester, b. p. 119°/18 mm., and *phenyl* ester, b. p. 187°/14 mm.

When heated for one hour with phosphorus pentachloride, hydropinenecarboxyl chloride yields α-*chloro*allocamphanecarboxyl (*chlorohydropinenecarboxyl*) *chloride*, $C_{10}H_{15}Cl\cdot COCl$, which sublimes with partial decomposition into hydrogen chloride and an unsaturated chloride. The chloro-chloride is obtained as a white, camphor-like mass, m. p. 118—119°, by evaporation of its ethereal solution after shaking with aqueous sodium carbonate. It probably consists of a mixture of two stereoisomerides related to one another as the *endo-* and *exo-*modifications of bornyl chloride. This view is supported by the behaviour of the *methyl* ester, which is obtained by boiling the chloro-chloride with methyl alcohol for fifteen hours, and apparently consists of two stereoisomerides of different stability, one of the isomerides readily losing hydrogen chloride on distillation, whilst the other is stable. The stable (presumably *exo-*) chloro-ester can be isolated from the mixture by repeated distillation under diminished pressure and has b. p. 131°/13 mm.

α-*Chloro*allocamphanecarboxyl*amide*, prepared from the chloro-chloride and ammonia in ethereal solution, has m. p. 122°, and when boiled with water loses hydrogen chloride, yielding an unsaturated *amide*, $C_{10}H_{15}\cdot CO\cdot NH_2$, which crystallises in lustrous leaflets, m. p. 210°, and when kept in contact with fuming hydrochloric acid overnight, is transformed into the original chloro-amide.

When boiled with methyl-alcoholic potassium hydroxide, methyl α-chloro*allo*camphanecarboxylate yields an oil which consists of a

mixture of hydropinenecarboxylic acid and two isomeric *camphene-carboxylic acids*. One of the latter acids has been isolated, and crystallises in needles, m. p. 105°, b. p. 149—151°/11 mm.

From the product of oxidation of the above acid mixture with potassium permanganate in alkaline solution, two isomeric *ketonic (camphenilonecarboxylic?) acids*, $C_{10}H_{14}O_3$, of m. p. 106° and 131°, together with a hydropinenecarboxylic acid of m. p. 71°, were isolated. The last-mentioned acid gave the same copper, lead, ferrous, ferric, mercuric and silver salts, and the same *anhydride* (microscopic, regular octahedra, m. p. 210°, b. p. 228°/16 mm.) as the original hydropinenecarboxylic acid of m. p. 78°, but differed from it in the magnitude and sign of its rotation ($[a]_D^{21}$ 11·29° in alcohol).

The ketonic acid of m. p. 106° forms a *semicarbazone* (decomp. 203°), and when boiled with acetic anhydride yields an *unhydride*, $C_{20}H_{26}O_5$, crystallising in leaflets, m. p. 114°.   F. B.

Ethyl p-Bromobenzoylacetate. WILLIAM J. HALE and LAMBERT THORP (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 132—137).—The preparation of dehydro-p-bromobenzoylacetic acid by the method employed by Perkin in the case of the unsubstituted acid (A., 1885, 277) is described.

p-Bromotoluene was oxidised by boiling permanganate to p-bromobenzoic acid; this was converted into the chloride, which was then condensed with ethyl sodioacetoacetate, and, finally, the sodium compound of ethyl p-bromobenzoylacetoacetate was gently warmed with aqueous ammonia. The resulting *ethyl p-bromobenzoylacetate*, $C_6H_4Br \cdot CO \cdot CH_2 \cdot CO_2Et$, was obtained as a heavy oil, which, in extremely small quantities, gives a deep red colour with ferric chloride. It could not be distilled, and, when boiled in an open tube, it gave a quantitative yield of *dehydro-p-bromobenzoylacetic acid*, $C_6H_4Br \cdot CO \cdot CH < ^{CO——O}_{CO \cdot CH} > O \cdot C_6H_4Br$, in the form of small, yellow needles from glacial acetic acid, m. p. 261°. *p-Bromobenzoylacetic acid*, $C_9H_7O_3Br$, was obtained by hydrolysing the ester with cold 3% potassium hydroxide in the form of needle-like plates which decompose at 106—107° into p-bromoacetophenone, and give a violet colour with ferric chloride.   J. C. W.

Spirans. III. Attempts to Prepare Optically Active Spirans and Asymmetric Rearrangement. HERMANN LEUCHS and JOHANNES WUTKE (*Ber.*, 1913, 46, 2420—2435. Compare Leuchs and Gieseler, A., 1912, i, 714).—In the preparation of bis-1-hydrindone-2:2-spiran from dibenzylmalonyl chloride, when aluminium chloride serves to eliminate hydrogen chloride, two by-products are obtained. The one, $C_{16}H_{13}Cl$, 1-chloro-2-benzylidene, m. p. 65°, amounts to 19% of the theoretical. The other is a yellow oil identified by means of its phenylhydrazone as 2-benzylhydrindone. Although only 10% have been separated, it amounts to 50% of the theoretical quantity.

When ferric chloride is substituted for aluminium chloride, a much better yield of the bishydrindonespiran is obtained. Its properties

are in accord with the formula $C_6H_4{<}^{CH_2}_{CO}{>}C{<}^{CH_2}_{CO}{>}C_6H_4$. It forms a diphenylhydrazone and a mono-oxime, and also reacts with two molecules of hydroxylamine, forming a dioxime dihydrate from which the excess of hydroxylamine oxidises away two atoms of hydrogen.

The mono-oxime (m. p. 215°) is converted by phosphorus pentachloride in ethereal suspension into an amide, either 1-hydrindone-dihydrocarbostyril-2 : 3-spiran or *iso*carbostyrilspiran. The mono-oxime shows no tendency to form an *iso*oxazole.

The 2-position of the carbonyl group in the spiran makes it possible to convert it into an acid, $C_{17}H_{14}O_3$,

$$CO_2H \cdot C_6H_4 \cdot CH_2 \cdot CH{<}^{CH_2}_{CO}{>}C_6H_4,$$
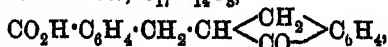
which when heated regenerates the spiran.

Semicarbazide acetate in cold alcoholic solution converts the spiran into an insoluble mixed hydrazide of the carbamic acid and the acid $C_{17}H_{14}O_3$, namely, $C_6H_4{<}^{\overline{\quad\quad\quad CH_2 \cdot CH \cdot CH_2}}_{CON_2H_2 \cdot CO \cdot NH_2 \quad CO-C_6H_4}$, from which the free acid is recovered.

Hydroxylamine yields an oximic acid,

$$CO_2H \cdot C_6H_4 \cdot CH_2 \cdot CH{<}^{\overline{CH_2\quad}}_{C(N \cdot OH)}{>}C_6H_4,$$
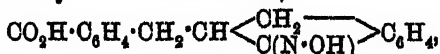
which can be easily reduced with sodium amalgam. Two hydrogen atoms are taken up, and a new asymmetric carbon atom formed, the hydroxy-acid having the formula

$$CO_2H \cdot C_6H_4 \cdot CH_2 \cdot CH{<}^{\overline{CH_2\quad}}_{CH(OH)}{>}C_6H_4,$$
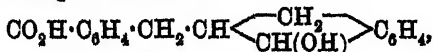
and being a mixture of two racemic forms. It does not tend to form an anhydride. The keto-acid is converted into the corresponding acid chloride by means of phosphorus pentachloride; this as low as 60° loses hydrogen chloride, and forms bishydrindonespiran.

Ammonia acts on the spiran to form two compounds—the one, $C_{17}H_{15}O_2N$, representing the amide of the ketonic acid, and the other, $C_{17}H_{13}ON$, being the corresponding nitrile,

$$CN \cdot C_6H_4 \cdot CH_2 \cdot CH{<}^{CH_2}_{CO}{>}C_6H_4.$$
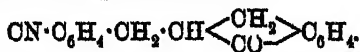
This constitution is confirmed by the fact that the action of ammonia on the keto-chloride gives rise to the same amide.

The amide is not hydrolysed by cold concentrated hydrochloric acid, but converted into an anhydride, which is hydrolysed by heating with 70% sulphuric acid at 170° to a spiran-anhydride.

Crystallisation of the brucine salt of the ketonic acid yields a theoretical yield of the optically active *dextro* salt, both the crystals and the mother liquor being dextrorotatory. It is assumed that the *laevo*-acid salt is enolised and the enol re-converted into the ketonic *d*-salt, since the equilibrium is determined entirely in this direction owing to the crystallisation of the *d*-salt as fast as it is formed.

The transformation is an instance of asymmetric rearrangement

rather than of autoracemisation, since the optically inactive enol gives rise exclusively to an optically active acid.

The *d*-ketonic acid slowly but completely loses its activity on keeping in chloroform solution, and still more quickly in neutral or alkaline aqueous solution, owing to conversion into the enol.

An optically active bishydrindonespiran could not be obtained by eliminating hydrogen chloride from the active keto-chloride.

Bishydrindonespirandioxime dihydrate forms colourless, slender needles, m. p. 175° (decomp.).

The Beckmann rearrangement product, $C_{17}H_{18}O_2N$, of the mono-oxime separates in long, colourless needles, m. p. 255° (decomp.); it gives no ferric chloride reaction.

The mixed *hydrazide* from the spiran and carbamic acid, $C_{18}H_{17}O_4N$, crystallises in short needles, m. p. 245° (decomp.).

The *oxime* of 1-hydrindone-2-benzyl-*o*-carboxylic acid forms dome-like prisms, m. p. 188° (decomp.).

The *amide*, prepared from the keto-chloride by the action of ammonia, has m. p. 138—140°, crystallising in massive, four-sided platelets.

The *brucine* salt of the *dextro*-ketonic acid forms transparent, massive crystals, m. p. 180—183°. The acid derived from it has $[\alpha]_D^{20} + 64°$ in chloroform. The pure active acid could not be obtained —a product evaporated at 20° had m. p. 128—141°, $[\alpha]_D^{20} + 56°$. In benzene the pure acid had $[\alpha]_D^{20} + 79°$; it racemises here more quickly than in chloroform.   E. F. A.

Spirans. IV. Stereochemical Treatment of the Keto-Enol Question. HERMANN LEUCHS (*Ber.*, 1913, **46**, 2435—2442. Compare Lapworth, T, 1904, **85**, 30; K. H. Meyer, A., 1911, i, 350, 940).—1-Hydrindone-2-benzyl-*o*-carboxylic acid when treated with bromine in chloroform solution readily forms a brominated ketonic acid, $CO_2H \cdot C_6H_4 \cdot CH_2 \cdot CBr {<}_{CO}^{CH_2}{>} C_6H_4$. Proof of this structure is afforded by the fact that on heating with ammonium hydroxide, the bromine is displaced and a lactone formed, namely, *dihydro*isocoumarin-1-*hydrindone*-3 : 2-*spiran*, $C_6H_4 {<}_{CO \cdot O}^{CH_2}{>} C {<}_{CO}^{CH_2}{>} C_6H_4$.

If in the process of bromination the first stage is the formation of an enol, $CO_2H \cdot C_6H_4 \cdot CH_2 \cdot C {<}_{C(OH)}^{CH_2}{>} C_6H_4$, which contains no asymmetric carbon atom, then on bromination of the optically active 1-hydrindone-2-benzyl-*o*-carboxylic acid, an optically inactive product should result.

Actually an optically active ($[\alpha]_D + 6\cdot5°$) product is obtained containing much inactive brominated keto-acid. Heating with sodium carbonate changes the sign of the rotation, and it was possible to isolate the pure 1-*dihydro*isocoumarin-1-*hydrindone*-3 : 2-*spiran*, which crystallises in lustrous needles, m. p. 175—176°, $[\alpha]_D^{20} - 65\cdot3°$.

This is the first optically active substance in which the spiran carbon atom is the asymmetric centre.

Bromination of ketones does not in consequence necessarily involve the intermediate formation of enol; in this case about 5—10% of

the brominated product is optically active. It is considered that even in this instance the greater part of the bromination involves the intermediate formation of the enol, and that this will be still more the case with substances which are more easily enolised.

2-*Bromo-α-hydrindone-2-benzyl-o-carboxylic acid* forms colourless crystals pointed at one end, m. p. 154° ; they are converted into the lactone on fusion.

Dihydroisocoumarin-1-hydrindone-3 : 2-*spiran* crystallises in needles or prisms, m. p. 153—154°. E. F. A.

Studies in Esterification. V. Esterification of Amides and Thioamides and the Formation of Dithio-esters. E. EMMET REID (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 423—430. Compare A., 1909, ii, 650 ; 1910, i, 481 ; 1911, i, 199 ; ii, 477).—In earlier papers it has been shown with reference to esterification that benzamide is the analogue of benzoic acid, and that mercaptan is the analogue of alcohol. It is now shown that benzamide can be esterified by mercaptan, and thiobenzamide by alcohol or mercaptan.

Ethyl thiolbenzoate is readily decomposed into mercaptan and benzamide by the action of ammonia at 20°, whereas ethyl benzoate reacts but slowly with ammonia even at 200°. Benzamide is readily esterified in presence of hydrochloric acid, which not only catalyses the reaction, but also combines with the ammonia so that the action proceeds to completion, and it was therefore expected that hydrogen chloride would similarly accelerate the esterification of benzamide by mercaptan. On heating benzamide in a sealed tube at 100° with mercaptan, saturated with hydrogen chloride at $-20°$, ethyl thiolbenzoate and ammonium chloride were produced. Thiobenzamide unites with about 1·5 mols. of hydrogen chloride to form an amber-coloured liquid, whilst other thioamides combine with about 1 mol.

Ethyl dithiobenzoate can be prepared by treating thiobenzamide, saturated with dry hydrogen chloride at 0°, with rather more than the calculated amount of mercaptan, and leaving the mixture in a sealed tube for about five weeks ; the ester has b. p. 180°/28 mm., D_{25}^{25} 1·1477, D_4^{25} 1·1439, apparent coefficient of expansion 0—25°, 0·000699, molecular volume, 159·28, viscosity at 25°, 0·03117, and fluidity at 25°, 32·09. Those constants are compared with those of ethyl benzoate and ethyl thiolbenzoate. Ethyl dithiobenzoate is readily transformed into thionbenzamide by alcoholic ammonia at the ordinary temperature. The reaction : $Ph \cdot CS \cdot NH_2 + C_2H_5 \cdot SH \rightleftharpoons Ph \cdot CS \cdot SEt + NH_3$ is therefore reversible. E. G.

Action of Potassium Xanthate on Halogen-malonic Acids. EINAR BIILMANN and ERIK HOST MADSEN (*Eighth Inter. Cong. App. Chem.*, 1912, 25, 339—342).—It has been shown in earlier papers (A., 1905, i, 625 ; 1906, i, 625, 626) that by the action of potassium xanthate on the halogen derivatives of certain organic acids, xanthyl derivatives are produced which, on treatment with ammonia, are converted into thiol acids. The action of potassium xanthate on bromomalonic, bromoisopropylmalonic, bromoethylmalonic, and bromobenzylmalonic acids has now been studied. These acids yield xanthyl derivatives which are very unstable, and from which pure xanthylmalonic acids

cannot be obtained. On heating the acidified solutions, the corresponding monobasic acids are produced, and in this way xanthylacetic, α-xanthylbutyric, and β-phenyl-α-xanthylpropionic acids have been isolated.

If the solutions of potassium xanthate and alkali halogenmalonates are acidified immediately after they have been mixed, an entirely different reaction takes place and dixanthyl is produced, thus: $2OEt \cdot CS \cdot SK + R \cdot CBr(CO_2K)_2 + 3HCl = OEt \cdot CS_2 \cdot CS_2 \cdot OEt + R \cdot CH(CO_2H)_2 + KBr + 3KCl$.

β-Phenyl-α-xanthylpropionic acid, $CH_2Ph \cdot CH(CO_2H) \cdot S \cdot CS \cdot OEt$, m. p. 89—90°, prepared by the action of potassium xanthate on sodium α-bromophenylpropionate, forms colourless crystals, and when treated with a mixture of aqueous ammonia and alcohol, is converted into *α-thiol-β-phenylpropionic acid*, $CH_2Ph \cdot CH(SH) \cdot CO_2H$, b. p. 184—187°/11—12 mm., m. p. 46°, which forms colourless crystals. By the action of copper sulphate on the alkali salts of this thiol acid, the latter is oxidised to *α-disulphido-β-phenylpropionic acid*,

$$[CH_2Ph \cdot CH(CO_2H)]_2S_2,$$
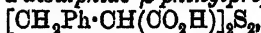
and the cuprous salt of the thiol acid is precipitated. The disulphido-acid can be obtained as a crystalline solid by oxidising the thiol acid with iodine.   E. G.

as-Phthalyl Chloride. JOHANNES SCHEIBER (*Ber.*, 1913, **46**, 2366—2370).—The author (A., 1912, i, 542, 559) has shown that the unsymmetrical formula, $C_6H_4{<}{}^{COl_2}_{CO}{>}O$, proposed for phthalyl chloride is untenable on both chemical and physical grounds, and Ott (A., 1912, i, 828) has obtained the isomeric asymmetric form of phthalyl chloride. The behaviour of the new chloride towards compounds of the type of ethyl sodioacetoacetate and towards ammonia has been now studied as well as the ultra-violet absorption spectra.

Both chlorides behave similarly with ethyl acetoacetate, since in each case reaction involves the formation of a compound

$$COCl \cdot C_6H_4 \cdot CO \cdot CHAc_2.$$
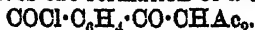
Hence the behaviour of such chlorides with sodium acetoacetate as also with ammonia gives no clue as to their structure.

Both chlorides give exclusively o-cyanobenzoic acid with ammonia, but the new asymmetric chloride reacts more slowly. There is thus a considerable difference in the stability of the complexes $C_6H_4{<}{}^{COl_2}_{SO_2}{>}O$ and $C_6H_4{<}{}^{COl_2}_{CO}{>}O$. The asymmetric chloride absorbs less strongly than phthalic acid or its esters in the ultra-violet.   E. F. A.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and Their Use for Synthetical Operations. IX. EMIL FISCHER and MAX RAPAPORT (*Ber.*, 1913, **46**, 2389—2401).—In part already abstracted (this vol., i, 731).

[With H. STRAUSS.]—*Trimethylcarbonatophloroglucinolcarboxylic acid*, obtained on treating phloroglucinolcarboxylic acid with methyl chloroformate in presence of dimethylaniline, forms small, colourless prisms,

m. p. 122° (decomp.), and no longer shows a bluish-violet coloration with ferric chloride. It is converted into the corresponding chloride by phosphorus pentachloride. E. F. A.

Pyrimidines. LV. The Catalytic Action of Esters in the Claisen Condensation. TREAT B. JOHNSON and ARTHUR J. HILL (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 147—156 *).—Ethyl phenoxy-acetate undergoes a Claisen condensation in ethereal solution in presence of sodium to form the sodium compound of ethyl $\alpha\gamma$-di-phenoxyacetoacetate, $OPh \cdot CH_2 \cdot CO \cdot CH(OPh) \cdot CO_2Et$. The same substance was produced in presence of ethyl acetate, and no evidence of the formation of the condensation product of the two esters, namely, ethyl γ-phenoxyacetoacetate, could be obtained. As has since been described (A., 1912, i, 912), the crude sodium salt condenses with thiocarbamide to form 2-thio-5-phenoxy-4-phenoxymethyltetrahydro-6-pyrimidone, and the yield of this insoluble product has been taken as an indication of the extent of the above Claisen condensation under different conditions. It is found that ethyl acetate acts as a catalyst, the addition of 0·5 mol. more than doubling the yield. J. C. W.

Some Derivatives of 4-Hydroxy*iso*phthalic Acid. FRANCIS D. DODGE (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 81—85).—During the steam-distillation of large quantities of methyl salicylate, the author has sometimes obtained, towards the end of the operation, crystals of dimethyl 4-hydroxy*iso*phthalate (Jacobsen, A., 1878, 583). Its presence is ascribed to irregularities in the manufacture of salicylic acid, since 4-hydroxy*iso*phthalic acid may be prepared by the action of carbon dioxide on sodium salicylate at 370° (Ost, A., 1876, 521).

Partial esterification of the acid and also partial hydrolysis of the dimethyl ester lead to the same *mono* ester, which crystallises in transparent plates with $1H_2O$ from diluted alcohol, has m. p. 187° when anhydrous, and gives a reddish-purple coloration with ferric chloride. From the fact that it yields methyl anisate on heating, and according to V. Meyer's ester law, it is the para-ester (annexed formula). J. C. W.
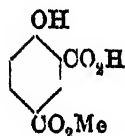
Carminic Acid. OTTO DIMROTH (*Annalen*, 1913, **399**, 1—35)—Investigations of the three "insect" dyes, carminic acid, kermesic acid, and laccaic acid, have been carried out concurrently in the expectation, which has been justified, that the results would mutually confirm one another. The structure of kermesic acid, which is the simplest of the three, has been determined (Dimroth and Scheurer, this vol., i, 980). The present paper, however, deals mainly with carminic acid. The remarkable and unexpected result has been established that this acid and kermesic acid are derivatives of an anthraquinone.

[With G. WEURINGH and L. HOLCH.]—Carminic acid, isolated from cochineal by Schunck and Marchlewski's process (it is advantageous, however, to decompose the lead lake by sulphuric acid and methyl, not

ethyl, alcohol), is oxidised by hydrogen peroxide and aqueous sodium hydroxide in the presence of a little cobalt sulphate as catalyst, whereby carminoquinone is formed as a labile intermediate product, the final product, after acidification with 80% acetic acid, being a sparingly soluble *sodium hydrogen* salt, $C_{26}H_{12}O_{16}Na_3,5H_2O$, yellow crystals. By trituration with dilute hydrochloric acid at 0° and crystallisation of the product from cold ethyl acetate, this salt yields 2 : 6-*dihydroxy-8-methyl-α-naphthaquinone*-3 : 5-*dicarboxylic acid*,

$$CO_2H \cdot C_6HMe(OH) \begin{smallmatrix} CO \cdot C \cdot OH \\ CO \cdot C \cdot CO_2H \end{smallmatrix},$$
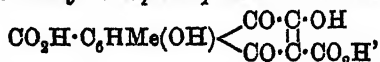
a pale yellow, extremely hygroscopic, crystalline powder, which forms a *sodium* salt, $C_{13}H_6O_8Na_3,4H_2O$, orange needles, and yields carminazarin by oxidation with potassium permanganate and sulphuric acid. The orientation of the substituents in the dicarboxylic acid is determined by its oxidation to carminazarin and by the colour reactions of the acid, which are identical with those of 2 : 6-dihydroxy-α-naphthaquinone (compare Dimroth and Kerkovius, following abstract). By gentle warming with water, the acid loses carbon dioxide and yields 2 : 6-*dihydroxy-8-methyl-α-naphthaquinone*-5-*carboxylic acid*,

$$C_{12}H_8O_6,$$
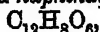
brownish-yellow needles (*potassium* salt, $C_{12}H_7O_6K$, citron-yellow needles ; *dipotassium* derivative, $C_{12}H_6O_6K_2$, orange-red crystals), which develops a red coloration with alkalis, brownish-yellow with concentrated sulphuric acid, and brownish-red with alcoholic ferric chloride. The monocarboxylic acid, which is obtained more conveniently by heating the sodium hydrogen derivative of the dicarboxylic acid with *N*-hydrochloric acid on the water-bath, reacts with bromine in glacial acetic acid at 40° to form 7-*bromo*-2 : 6-*dihydroxy-8-methyl-α-naphthaquinone*-5-*carboxylic acid*, $C_{12}H_7O_6Br$, m. p. 240—244°, yellow needles. The brominated acid forms α-bromocarmin by treatment with hydrobromic acid, and Will and Leymann's β-bromocarmin by treatment with bromine in cold methyl alcohol ; the latter is thus definitely proved to be 3 : 5 : 7-tribromo-2 : 6-dihydroxy-8-methyl-α-naphthaquinone.

The constitution, 2 : 3 : 6-trihydroxy-8-methyl-α-naphthaquinone-5-carboxylic acid, previously ascribed by the author to carminazarin, is supported by the fact that its oxidation product, carminazarinquinone, reacts with alcoholic *o*-phenylenediamine to form a *diphenazine*,

$$C_{24}H_{14}O_3N_4,$$
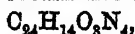
yellow needles, the *acetyl* derivative, $C_{26}H_{16}O_4N_4$, of which still forms a sparingly soluble *sodium* salt.

[With B. KERKOVIUS.]—The largest, well characterised fission product of carminic acid is coccinin, obtained by Hlasiwetz and Grabowski in 1867 by fusing the acid with potassium hydroxide. Prepared at 170—200° by a modification of these authors' process, coccinin, $C_{17}H_{14}O_6$, has been obtained as a crystalline substance which forms a *tetra-acetyl* derivative, $C_{25}H_{22}O_{10}$, m. p. 242—244°, faintly yellow crystals. By oxidation in 6% sodium hydroxide with air or oxygen until the colour of the solution has changed from yellow through green to a pure violet, and then acidifying with hydrochloric acid, coccinin

yields *coccinone*, $C_{17}H_{12}O_7$, dark brown, metallic crystals, which begins to decompose at 250°, and forms a *triacetyl* derivative, $C_{23}H_{18}O_{10}$, m. p. 210°, orange-red crystals, and three *barium* salts, one of which crystallises in glistening leaflets, and has a composition,

$$2C_{17}H_{10}O_7Ba,(C_{17}H_{11}O_7)_2Ba,$$
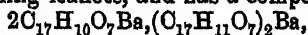
analogous to that of the sodium hydrogen salt of 2 : 6-dihydroxy-8-methyl-α-naphthaquinone 3 : 5-dicarboxylic acid. In concentrated sulphuric acid, coccinone develops a violet colour which changes to blue on the addition of boric acid—a reaction similar to those exhibited by most hydroxyanthraquinones.

Coccinone is reduced to coccinin by zinc dust and ammonia, and is oxidised by hydrogen peroxide and aqueous sodium hydroxide below 20°, yielding cochenillic acid and a second, unexamined acid. The author is of opinion that coccinin and coccinone are derivatives of anthranol and of anthraquinone respectively. The formation of cochenillic acid determines the orientation of a hydroxyl, methyl, and carboxyl group in coccinone which, therefore, receives the constitution

$$C_6HMe(OH)_2 {<}^{CO \cdot C \cdot CMe \Equals CH}_{CO \cdot C \cdot C(CO_2H):C \cdot OH},$$ whilst coccinin is regarded as

$$C_6HMe(OH)_2 {<}^{CH \text{—} C \cdot CMe \Equals CH}_{C(OH) \cdot C \cdot C(CO_2H):C \cdot OH} \text{ or}$$

$$C_6HMe(OH)_2 {<}^{C(OH) \cdot C \cdot CMe \Equals CH}_{CH \text{—} C \cdot C(CO_2H):C \cdot OH}.$$
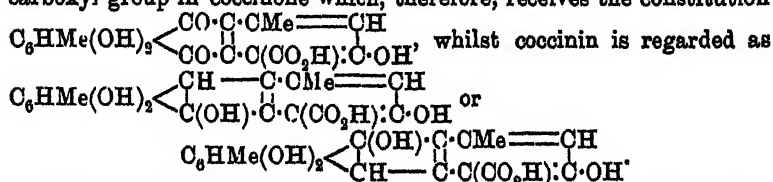
By heating with water at 200° or with dilute sulphuric acid at 170°, coccinone loses carbon dioxide and yields *decarboxycoccinone*,
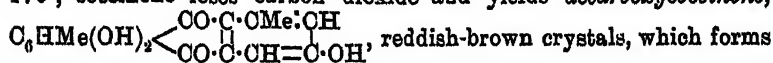
$$C_6HMe(OH)_2 {<}^{CO \cdot C \cdot CMe:CH}_{CO \cdot C \cdot CH=C \cdot OH},$$ reddish-brown crystals, which forms a purplish-red solution in alkalis, and dissolves in concentrated sulphuric acid with a blue colour changing to violet after the addition of boric acid.

[With L. HOLCH.]—The question remains to be discussed whether carminic acid is a derivative of anthraquinone, or whether the anthracene nucleus in coccinin is produced during the fusion of carminic acid with potassium hydroxide. By distillation with zinc dust in a current of hydrogen, carminic acid yields about 5% of a mixture of hydrocarbons which apparently contains anthracene and α-methylanthracene, since in the mixture, after oxidation, anthraquinone has been certainly identified, whilst a substance, m. p. 165°, has also been obtained which has the very characteristic crystalline form of α-methylanthraquinone.

When boiled with dilute sulphuric acid, carminic acid yields about 10% of a *trihydroxymethylanthraquinonecarboxylic acid*, $C_{16}H_{10}O_7$, m. p. above 305° which crystallises in needles, and is converted by water at 230—240° into a *trihydroxymethylanthraquinone*, $C_{15}H_{10}O_5$, brick-red needles. C. S.

2 : 6- and 2 : 7-Dihydroxy-α-naphthaquinones. OTTO DIMROTH and BERTHOLD KERKOVIUS (*Annalen*, 1913, 399, 36—43).—By treatment with acetic anhydride containing a few drops of concentrated sulphuric acid, 6-hydroxy-β-naphthaquinone yields 1 : 3 : 4 : 6-*tetra-*

acetoxynaphthalene, $C_{18}H_{18}O_8$, m. p. 181—182°, colourless leaflets. By hydrolysis with methyl-alcoholic potassium hydroxide, the passage of oxygen through the resulting solution, and acidification, 2 : 6-*dihydroxy-a-naphthaquinone*, $C_{10}H_6O_4$, yellow crystals, is obtained. It forms a *diacetyl* derivative, yellow leaflets, and dissolves in sodium carbonate and sodium hydroxide with a blood-red colour, and in concentrated sulphuric acid with a brownish-yellow colour. By bromination in glacial acetic acid, 2 : 6-dihydroxy-a-naphthaquinone forms a *dibromo*-derivative, $C_{10}H_4O_4Br_2$, m. p. 283—286°, yellowish-brown crystals, which is converted by bromine in methyl alcohol into 3 : 5 : 7-*tribromo*-2 : 6- *dihydroxy - a - naphthaquinone*, $C_{10}H_3O_4Br_3$, m. p. 242°, yellow crystals ; the latter dissolves in sodium carbonate or hydroxide, or in concentrated sulphuric acid, with a reddish-brown colour.

By reactions similar to the preceding, 7-hydroxy-β-naphthaquinone has been converted into 1 : 2 : 4 : 7-*tetra-acetoxynaphthalene*, m. p. 140—141°, colourless crystals, from which 2 : 7-*dihydroxy-a-naphthaquinone*, decomp. above 200°, orange-yellow needles, has been obtained. The latter dissolves in aqueous sodium hydroxide and in concentrated sulphuric acid with a crimson-red colour, and by bromination in glacial acetic acid yields 3 : 6 : 8-*tribromo*-2 : 7-*dihydroxy-a-naphthaquinone*, m. p. 228—229°, pale yellow prisms, the solution of which in sodium carbonate or hydroxide is much more blue than that of the preceding isomeride.

Mention has been made (Dimroth, preceding abstract) of the importance of the preceding colour reactions in connexion with the constitutions of β-bromocarmin and of 2 : 6-dihydroxy-8-methyl-*a*-naphthaquinone-5-carboxylic acid.

C. S.

Kermes Dye. OTTO DIMROTH and WILHELM SCHEURER (*Annalen*, 1913, **399**, 43—61).—In addition to kermesic acid, kermes dye contains about 0·06% of a second acid, $C_{18}H_8O_8$, which is called *flavo-kermesic acid*. It crystallises in needles or prisms. In the optical properties of its solutions and as a dye, it shows very little resemblance to kermesic acid, and, therefore, has not been studied thoroughly. The separation of flavokermesic acid from kermesic acid is effected best by utilising the facts that the disodium salt of the latter is almost insoluble in hot 2*N*-sodium acetate, whilst sodium flavokermesate dissolves fairly easily. The presence of flavokermesic acid in kermesic acid is easily detected by the colour of the solution in concentrated sulphuric acid containing boric acid ; the solution of the pure acid is a clear blue, that of the impure acid is dull, or a dirty bluish-violet.

When heated with water at 150°, kermesic acid loses carbon dioxide, and is converted into *decarboxykermesic acid*, $C_{17}H_{12}O_7$, red needles, which begins to sublime above 150°, carbonises without melting, is almost insoluble in sodium hydrogen carbonate, and dissolves in aqueous sodium hydroxide and in concentrated sulphuric acid containing boric acid, forming solutions which have the same colours as the corresponding solutions of kermesic acid. Kermesic acid yields a-bromocarmin by bromination in boiling 50% acetic acid. When brominated in boiling glacial acetic acid, however, it is converted into

bromococcin, $C_{16}H_9O_8Br$, m. p. 259—260° (decomp.), red needles, which forms a *potassium hydrogen* salt, $C_{16}H_8O_8BrK, C_{16}H_9O_8Br$, and a *tetra-acetyl* derivative, $C_{16}H_5O_8BrAc_4$, yellow crystals, and yields cochenillic acid by oxidation with warm alkaline hydrogen peroxide in the presence of a trace of a manganous salt. These results indicate that bromococcin must have the constitution

$$C_6Br(OH)_3 \diagdown \genfrac{}{}{0pt}{}{CO \cdot C \cdot CMe \!=\!\!=\! CH}{CO \cdot C \cdot C(CO_2H) : C \cdot OH}$$
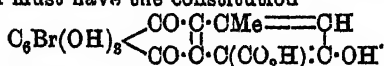
The three homonuclear hydroxyl groups cannot be in the vicinal position because bromococcin resembles purpurin, not anthragallol, in its dyeing function.

When kermesic acid or bromococcin is brominated in methyl alcohol and the product is treated with concentrated hydrobromic acid, *tribromococcin*, $OH \cdot C_6MeBr_2 \diagup \!\!\!\diagdown \genfrac{}{}{0pt}{}{CO}{CO} \diagdown \!\!\!\diagup C_6Br(OH)_3$, m. p. 245—248° (decomp.), is obtained, which crystallises from acetic acid in long, red needles. It dissolves in concentrated sulphuric acid with a reddish-violet colour, which changes to deep blue by the addition of boric acid. It forms a *tetra-acetyl* derivative, $C_{15}H_8O_6Br_3Ac_4$, m. p. 223°, greenish-yellow needles, and is converted into nitrococcusic acid by fuming nitric acid. A *substance*, $C_{16}H_6O_5Br_4$, yellow needles, is obtained as a by-product in the preparation of tribromococcin.

Kermesic acid, $C_{18}H_{12}O_9$, and bromococcin, $C_{16}H_9O_8Br$, are nearly related substances. Hence from the constitution of the latter, it is very probable that kermesic acid, which does not exhibit the properties of an aldehyde, has the constitution

$$C_6Ac(OH)_3 \diagdown \genfrac{}{}{0pt}{}{CO \cdot C \cdot CMe \!=\!\!=\! CH}{CO \cdot C \cdot C(CO_2H) : C \cdot OH}$$
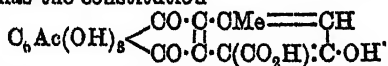
This deduction is supported, not only by the formation of tribromococcin by bromination, but also by the result of the distillation of kermesic acid with zinc dust. The mixture of hydrocarbons thus obtained contains α-methylanthracene (isolated as the styphnic acid compound, and identified in the form of α-methylanthraquinone) and, probably, anthracene.

[With A. E. Sherndal.]—The wax which is obtained in working up the kermes dye is *ceryl cerotate*, $C_{52}H_{104}O_2$, m. p. 81°, colourless leaflets, since it yields ceryl alcohol and cerotic acid by hydrolysis.

C. S.

Stick-lac Dye. Otto Dimroth and Stephan Goldschmidt (*Annalen*, 1913, **399**, 62—90).—Stick-lac or gum-lac contains, embedded in resin, wax, and other substances, a small quantity of a red dye similar to cochineal. The dye has been called laccaic acid. It is not, as supposed formerly, identical with carminic acid, but the two are closely related, giving solutions in alkalis of the same colour and exhibiting the same spectrum ; the characteristic absorption bands shown by the two acids in concentrated sulphuric acid, however, are differently situated in the two spectra.

Laccaic acid is isolated as follows : Stick-lac is digested with water at 50°, the clear red solution when cold, is acidified with acetic acid,

decanted from the precipitated resin, evaporated to a small bulk, and acidified with hydrochloric acid ; the crude laccaic acid thus obtained is crystallised from hot 85% formic acid, washed, dried at 60—70°, and finally crystallised from hot dilute hydrochloric acid. It has the formula $C_{20}H_{14}O_{10}$, not $C_{16}H_{12}O_8$ as stated in the literature, crystallises in dark red, microscopic rhombohedra, decomposes and yields a trace of a red sublimate when heated, and does not form crystalline salts except a *sodium hydrogen* salt, $C_{20}H_{12}O_{10}Na_2, C_{20}H_{13}O_{10}Na$. Its dyeing properties are similar to those of carminic acid. Laccaic acid neutralises five equivalents of barium hydroxide, and when treated with acetic anhydride and a few drops of concentrated sulphuric acid yields a *triacetyl* derivative, $C_{20}H_{20}O_{13}, C_2H_4O_2$, m. p. 176°, reddening at about 160°, yellow, microscopic needles (from acetic acid).

By reduction with tin and hydrochloric acid or with zinc dust and boiling aqueous ammonia, laccaic acid is converted into a *substance*, $C_{20}H_{16}O_9$, brownish-yellow rhombohedra, which is oxidised by hydrochloric acid and cupric chloride to a *substance*, $C_{20}H_{14}O_9$, which differs from laccaic acid in its colour reactions ; the substances $C_{20}H_{16}O_9$ and $C_{20}H_{14}O_9$ are probably related as quinol and quinone.

An alkaline solution of laccaic acid is readily oxidised by hydrogen peroxide in the presence of a trace of a cobalt, manganese, cerous, or ferrous salt. When one molecular proportion of hydrogen peroxide is used, the solution contains an unstable intermediate oxidation product, since by acidifying the solution and adding sulphurous acid, laccaic acid is recovered. The complete oxidation requires 2·5 to 3 molecular proportions of hydrogen peroxide, manganous chloride being the best catalyst. The oxidation product thus obtained is *calaic acid*, $C_{18}H_{14}O_{11}$, which crystallises from ether in small, yellow prisms containing ether of crystallisation and from water in needles containing $2\frac{1}{2}H_2O$. Calaic acid contains three carboxyl groups and one carbonyl group, does not possess dyeing properties, and forms a crystalline *barium* salt (by means of which it is best purified) and a *silver* salt, $C_{18}H_{12}O_{11}Ag_2$.

By bromination in glacial acetic acid, calaic acid yields two products. One of these is an *a-ketonic acid*, $C_{12}H_{10}O_6Br_2$, m. p. 208—209°, brownish-yellow crystals, which forms a *phenylhydrazone* and *semicarbazone*, develops a dirty reddish-violet coloration with ferric chloride, and by treatment with methyl-alcoholic hydrogen bromide yields an additive *compound* of the *methyl* ester, $C_{13}H_{12}O_6Br_2, HBr$, m. p. 133—134° (decomp.), colourless needles. When heated with concentrated sulphuric acid at 80—90°, the ketonic acid loses carbon monoxide and yields an *acid*, $C_{11}H_{10}O_5Br_2$, m. p. 245—246° (decomp.), which is monobasic and develops an intense violet coloration with ferric chloride.

The second and more important product of the bromination of calaic acid is *β-bromolaccain*, $C_{12}H_5O_8Br$, which is separated from the other product by means of its solubility in cold acetone. β-Bromolaccain has m. p. 234—235° (decomp.), separates from aqueous solution in stout crystals containing $2H_2O$, and forms a *potassium* salt,

$$C_{12}HO_8BrK_4, H_2O,$$

hexagonal plates. It develops a deep red coloration with ferric

chloride, dyes wool reddish-yellow in an acid-bath, and by treatment with acetic anhydride and concentrated sulphuric acid forms *diacetyl-β-bromolaccain anhydride*, $C_{16}H_7O_9Br$; the last reaction proves that β bromolaccain contains two carbonyl groups in the ortho-position and two hydroxyl groups.

Since β-bromolaccain presents in its behaviour a close analogy to β-bromocarmin and resembles 2 : 6-dihydroxy-α-naphthaquinone in its colour reactions (Dimroth and Kerkovius, preceding abstract), there can be little doubt that its constitution is

$$CO_2H \cdot C \vdots C(CO_2H) \cdot C \cdot CO \cdot C \cdot OH$$
$$OH \cdot C = CH \cdot C \cdot CO \cdot CBr$$
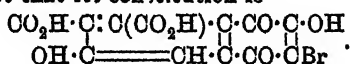
This is supported by the following evidence. Just as β-bromocarmin yields the indone derivative, α-bromocarmin, so β-bromolaccain in boiling aqueous solution yields with bromine, *a-bromolaccain*,

$$CBr_2 {<}^{CO \cdot C \cdot C(CO_2H) \vdots CBr}_{CO \cdot C \cdot CBr = C \cdot OH}$$
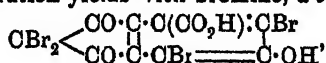
colourless needles, which decomposes when heated and yields bromoform and 2 : 6-*dibromophenol* 3 : 4 : 5-*tricarboxylic acid*, m. p. 257—258°, by treatment with sodium hypobromite; the tricarboxylic acid develops only a faint coloration with ferric chloride (therefore, the hydroxyl group is not in the ortho-position to a carboxyl group) and as a phthalic acid derivative yields a yellow dye by fusion with resorcinol and zinc chloride.

The constitution of β-bromolaccain is also supported by the fact that oxidation by hydrogen peroxide in glacial acetic acid on the water-bath produces *hydroxytricarboxyphenylglyoxylic acid*,

$$OH \cdot C_6H(CO_2H)_3 \cdot CO \cdot CO_2H,$$
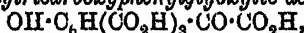
m. p. 229·5—230° (decomp.), flattened plates, which develops a brownish-red coloration with ferric chloride and is converted into a *phenol-tetracarboxylic acid*, m. p. 212—214° (decomp.), quadratic crystals, by concentrated sulphuric acid at 130—140°.

A by-product of the oxidation of β-bromolaccain is a *substance*, $C_{12}H_6O_9Br_2$, m. p. 188—190° (decomp.), which readily loses bromine and probably has the constitution

$$CBr_2 {<}^{C(OH)(CO_2H) \cdot C \cdot C(CO_2H) \vdots C \cdot CO_2H}_{CO = C \cdot CH = C \cdot OH}$$ C. S.
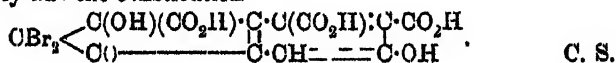
[Angeli-Rimini Reaction of the Aldehydes] ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 851—854).—A reply to Balbiano (this vol , i, 733).   R. V. S.

The New Decomposition of the Oximes. ANGELO ANGELI and LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 735—744. Compare Angeli, A., 1912, i, 269).—Benzophenoneoxime decomposes rapidly at about 180°, yielding benzophenone, nitrogen and ammonia. The decomposition occurs at a lower temperature (140°) in presence of copper oxide, whilst with cuprous chloride it begins a little above 100°. It was not possible to isolate a copper salt, but the *silver* salt was prepared. It is stable when dry, but if kept in a moist state in

the absence of air it evolves pure nitrogen, and benzophenone is formed at the same time.

The *silver* salt of piperonaldehydeoxime behaves similarly.

Fluorenoneoxime also decomposes at its m. p. ($194°$); the gas evolved contains nitric oxide as well as nitrogen, even when the decomposition is effected in the absence of air.

The mixture of stereoisomeric oximes prepared from phenyl *p*-tolyl ketone (m. p. about $120°$) decomposes above $200°$ in a like manner, nitric oxide being also formed.

In the case of deoxybenzoinoxime and acetophenoneoxime decomposition is slight when the pure substance is heated, but becomes considerable in presence of cuprous chloride or of cupric oxide.

Benzophenoneoxime, phenyl *p*-tolyl ketoneoxime, and acetophenoneoxime are apt to decompose spontaneously on keeping.   R. V. S.

Phototropy. FERDINANDO GRAZIANI and F. BOVINI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 793—797).—The authors have prepared a number of diphenylhydrazones and *p*-ditolylhydrazones, none of which is phototropic. In some cases in which the compounds had been previously prepared, the m. p.'s were found somewhat different from those given in the literature. Benzaldehydediphenylhydrazone has m. p. $125°$.

Anisaldehydediphenylhydrazone, $NPh_2 \cdot N{:}CH \cdot C_6H_4 \cdot OMe$, forms colourless crystals, m. p. $76°$.

Cuminaldehydediphenylhydrazone has m. p. $80—81°$.

Salicylaldehydediphenylhydrazone has m. p. $139—140°$.

Benzaldehyde-p-ditolylhydrazone, $N(C_7H_7)_2 \cdot N{:}CHPh$, crystallises in small, yellow prisms, m. p. $99°$.

Anisaldehyde-p-ditolylhydrazone, $N(C_7H_7)_2 \cdot N{:}CH \cdot C_6H_4 \cdot OMe$, forms large, flat needles, m. p. $128°$.

Cuminaldehyde-p-ditolylhydrazone, $N(C_7H_7)_2 \cdot N{:}CH \cdot C_6H_4 \cdot CHMe_2$, crystallises in long, silky needles, m. p. $104°$.

Cinnamaldehyde-p-ditolylhydrazone, $N(C_7H_7)_2 \cdot N{:}CH \cdot CH{:}CHPh$, forms flat, deep yellow needles, m. p. $143°$.

Salicylaldehyde-p-ditolylhydrazone, $N(C_7H_7)_2 \cdot N{:}CH \cdot C_6H_4 \cdot OH$, is a greenish-yellow, crystalline powder, m. p. $126°$.

Piperonaldehyde-p-ditolylhydrazone, $N(C_7H_7)_2 \cdot N{:}CH \cdot C_6H_3 \cdot O_2{:}CH_2$, forms colourless leaflets, m. p. $134°$.   R. V. S.

Tetra-alkylation of 1-Methyl*cyclo*hexanone. ALBIN HALLER (*Compt. rend.*, 1913, **157**, 179—185. Compare this vol., i, 629).—Whilst the alkylation of *cyclo*hexanone by means of sodamide proceeds but difficultly, methyl*cyclo*hexanone readily undergoes progressive alkylation. Thus 1-methyl*cyclo*hexan-6-one dissolved in ether, treated with sodamide, followed by the addition of methyl iodide, readily yields 1 : 5-dimethyl*cyclo*hexan-6-one, b. p. $170—171°$ (corr.), D_4^{18} $0·9146$, n_D^{18} $1·4508$ (compare Wallach, this vol., i, 482), together with a very small amount of the 1 : 1-isomeride. Further alkylation of the 1 : 5-compound yields 1 : 1 : 5-*trimethylcyclohexan-6-one*, b. p. $178—179°/755$ mm. (corr.), D_4^{18} $0·9043$, n_D^{18} $1·4493$, yielding in its turn 1 : 1 : 5 : 5-*tetra*methyl*cyclo*hexan-6-one (*loc. cit.*). The corresponding alcohols are

obtained by reduction with sodium in absolute alcohol. 1 : 5-*Dimethyl-cyclohexan-6-ol*, a viscous liquid with an odour like eugenol, has b. p. 174·5—175·5°/748 mm. (corr.), D_1^{20} 0·9235, n_D^{20} 1·4628. 1 : 1 : 5-*Trimethylcyclohexan-6-ol* has a similar odour, b. p. 186—187°/753 mm. (corr.), D_1^{20} 0·9128, n_D^{20} 1·4600.

Ethyl derivatives have been similarly prepared from 1-methyl*cyclo*hexan-6-one, the first stage giving 1-*methyl-5-ethylcyclohexan-6-one*, b. p. 194—196°/745 mm. (corr.), D_4^{20} 0·9162, n_D^{20} 1·4555. This then yields 1-*methyl-1 : 5-diethylcyclohexan-6-one*, b. p. 222—224°/757 mm. (corr.), D_4^{20} 0 9054, n_D^{20} 1·4572, and finally 1-*methyl-1 : 5 : 5-triethylcyclohexan-6-one*, b. p. 249—252°/765 mm. (corr.), b. p. 123—126°/16 mm. (corr.), D_4^{20} 0·9132, n_D^{20} 1·4634.

The corresponding alcohols have been prepared by reduction.

1-*Methyl-5-ethylcyclohexan* 6-*ol*, b. p. 202—204°/761 mm. (corr.), D_4^{20} 0 9268, n_D^{20} 1·4689.

1-*Methyl-1 : 5-diethylcyclohexan-6-ol*, b. p. 232—235°/749 mm. (corr), D_4^{20} 0 9206, n_D^{20} 1·473.

1-*Methyl-1 : 5 : 5-triethylcyclohexan-6-ol*, b. p. 258—260°/759 mm. (corr.), D_4^{20} 0·9255, n_D^{20} 1·4769.

The successive introduction of methyl groups into *cyclo*hexanone elevates the boiling point progressively, whilst causing a diminution in the density and the index of refraction, the same holding good for the corresponding alcohols.

The introduction of ethyl groups into methyl*cyclo*hexan-6-one produces a steady rise in the boiling point, whilst the density diminishes for the first two stages and increases at the third, the refractive index showing steady rise throughout. The same remarks apply to the corresponding alcohols. W. G.

Interaction of Diketones and Acid Amides. L. H. FRIEDBURG (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 131).—When molecular quantities of pure benzil and benzamide are distilled, a quantitative yield of benzonitrile, together with benzaldehyde and benzoic acid, is obtained. J. C. W.

Oxidation of Hydroxy*peri***naphthindenone. III.** GIORGIO ERRERA (*Gazzetta*, 1913, **43**, i, 583—594. Compare Errera and Cuffaro, A., 1912, i, 273).—The paper deals with some derivatives of hydroxy*peri*naphthindenone obtained from a substance mentioned in a former paper (A., 1911, i, 465) as having been prepared by the action of phenylhydrazine on hydroxy*peri*naphthindenone. The constitution of this substance is still being investigated. It

dissolves in bromine water, yielding the *hydrate* of *peri*naphthindantrione (annexed formula) (compare Ruhemann, T., 1911, **99**, 1146), which forms golden-yellow, prismatic crystals. These begin to decompose at about 110°, yielding the anhydrous *peri*naphthindantrione, which forms red crystals, m. p. about 273° (decomp.). The hydrate dissolves in cold concentrated sodium carbonate, yielding a white, crystalline *substance* from which acids regenerate the triketone. The hydrate yields a *sodium bisulphite*
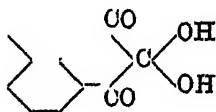
compound; hydroxylamine and phenylhydrazine do not give oxime or hydrazone, but reduce the substance. Both the hydrate and the anhydrous ketone readily yield an *alcoholate*, $C_{15}H_{12}O_4$, which crystallises in yellow, triclinic plates. The triketone reacts with *o*-phenylenediamine with production of the *phenazine*, $C_{19}H_{10}ON_2$, which crystallises in golden-yellow needles, m. p. 255—256°. The phenazine yields a *hydrazone*, $C_{25}H_{16}N_4$, crystallising in violet laminæ, m. p. about 299° (decomp.).
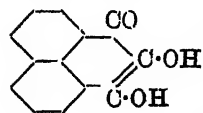
Reduction of the triketone (best with phenyl-hydrazine) leads to the formation of *dihydroxy*peri-naphthindenone (annexed formula), which can also be prepared by boiling the substance from phenylhydrazine and hydroxy*peri*naphthindenone with alcohol and sulphuric acid for six hours. Dihydroxy*peri*naphthindenone crystallises in silky, red needles, m. p. 258—259° (sintering previously). The *potassium* salt,

$$C_{13}H_7O_3K,H_2O,$$
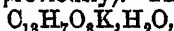
resembles permanganate in appearance. The salts of the substance are stable in the solid state, but are readily oxidised by air when in solution, yielding eventually naphthalic anhydride. Oxidation with bromine water regenerates the triketone. Conversely, the latter substance is partly reduced to dihydroxy*peri*naphthindenone when boiled with water. The author suggests that the blue coloration observed by Ruhemann (T., 1910, **97**, 2027) when triketohydrindene is treated with potassium hydroxide is probably due to the transitory appearance of hydroxydiketohydrindene in its tautomeric form.

On esterification with methyl sulphate, dihydroxy*peri*naphthindenone yields a *monomethyl ether*, $C_{14}H_{10}O_3,H_2O$, crystallising in golden-yellow leaflets or needles, which on heating melt and lose water below 100°, giving the anhydrous substance, m. p. 115—135°. The *dimethyl ether*, $C_{15}H_{12}O_3$, is obtained by the same method, and forms golden-yellow needles, m. p. 84—85°. The *dibenzoyl* derivative, $C_{27}H_{16}O_5$, crystallises in greenish-yellow prisms, m. p. 217—218°.   R. V. S.

Improved Method for the Production of β-Aminoanthra-quinone. M. L. Crossley (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 351—352).—β-Aminoanthraquinone has been obtained by Bourcart and also by Perger by heating sodium anthraquinone-β-sulphonate with solution of ammonia (25%) in a sealed glass tube. This method has now been found unsuitable for the preparation of the compound, as it is dangerous and gives only a small yield. A modified method has therefore been devised in which the reagents are heated at 190° in an iron tube, and the yield increased from 14% to 45%. When the ammoniacal filtrate from the β-aminoanthraquinone is acidified with hydrochloric acid, a brown precipitate is obtained which shows strong tinctorial properties with animal fibres.   E. G.

Syntheses in the Terpene Group. William H. Perkin, jun. (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 224—264).—A review of the chemistry of the known and possible menthenols and menthadienes with special reference to the syntheses accomplished by Perkin and his collaborators.   J. C. W

Terpenes. Polymerisation of Pinene. GEORGE B. FRANKFORTER and F. W. POPPE (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 363—369). —By the action of iodine on pinene in presence of aluminium iodide, a pinene *hydriodide*, b. p. 107°/7 mm., D 1·447, and n_D 1·6245, is produced, together with a *di-iodide*, $C_{10}H_{16}I_2$, b. p 119—125°/7 mm., D 1·69. Both the hydriodide and di-iodide are decomposed by light with formation of dipinene and colophonene.

Dipinene, $(C_{10}H_{16})_2$, b. p. 172°/7 mm., D_{20} 0·947, n_D^{20} 1·52517, is optically inactive, and has a viscosity 101 at 25° as compared with water. *Colophonene*, $(C_{10}H_{16})_4$, m. p. 102—103°, is a pale yellow, crystalline substance; it yields two *tetrachloro*-derivatives, $(C_{10}H_{15}Cl)_4$, one, m. p. 119—121°, obtained by treating it with potassium permanganate and hydrochloric acid, and the other, m. p. 99—102°, obtained by the action of sulphuryl chloride. Both dipinene and colophonene are remarkably stable. E. G.

Constituents of Essential Oils. Reductions in the Sesquiterpene Group. FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1913, **46**, 2303—2308). — Eudesmone, b. p. 122—124°/7 mm., D^{20} 0·91964, n_D 1·50874, $[\alpha]_D$ +54·6°, obtained by the action of alcoholic potassium hydroxide on eudesmene dihydrochloride (which is produced when eudesmol is treated with hydrogen chloride in acetic acid solution; compare Semmler and Tobias, this vol., i, 885), can be reduced in acetic acid by free hydrogen under the catalytic influence of platinum black, producing *tetrahydroeudesmene*, $C_{15}H_{28}$, b. p. 122—122·5°/7·5 mm., D^{20} 0·8893, n_D 1·48278, $[\alpha]_D$ +10·2°.

Similar reduction of purified eudesmol, needles, m. p. 84°, not only removed the ethylenic linkings, but also affected the hydroxyl group, for the product is a *hydrocarbon*, $C_{15}H_{28}$, b. p. 117°/5·5 mm., D^{20} 0·8896, n_D 1·48425, $[\alpha]_D$ +11·8°; this is strikingly different from the result of reduction in ethereal solution (*loc. cit.*), the product of which is dihydroeudesmol, $C_{15}H_{28}O$.

The action of ozone on eudesmene in acetic acid solution gave decided indications of the distinct natures of eudesmene and selinene; one of the products was a *substance*, b. p. 180—200°/7 mm., D^{20} 1 081, n_D 1·49429, $[\alpha]_D$ +13°, which yields a *semicarbazone*.

Catalytic reduction of guajol, m. p. 91°, in acetic acid solution by free hydrogen resulted in the simultaneous elimination of the ethylenic linkings and the hydroxyl group with the formation of *tetrahydroguajene*, $C_{15}H_{28}$, b. p. 118—119°/7 mm., D^{20} 0·8806, n_D 1·47840, $[\alpha]_D$ +10·6°.

Reduction of tricyclic α-santalol, b. p. 147—148°/4·5 mm., D^{20} 0·9745, n_D 1·50552, $[\alpha]_D$ +0·6°, in a similar manner yielded almost quantitatively a bicyclic *tetrahydrosantalene*, $C_{15}H_{28}$, b. p. 115—116°/9 mm., D^{20} 0·8655, n_D 1·46908, $[\alpha]_D$ +5·6°, not only the ethylenic linkings and the hydroxyl group, but also one of the rings having been eliminated. Reduction of bicyclic β-santalol, b. p. 158—158·5°/5 mm., D^{20} 0·97174, n_D 1·51357, $[\alpha]_D$ −41·8°, yielded a product, b. p. 119°/10 mm., D^{20} 0·8550, n_D 1·46612, $[\alpha]_D$ +2·8°, which is mainly a *tetrahydrosantalene*, $C_{15}H_{28}$, probably containing a small quantity of a hexahydrosantalene due to a little monocyclic santalol, $C_{15}H_{24}O$, in the starting

product; at the same time in the reduction a bicyclic saturated alcohol, $C_{15}H_{26}O$, was obtained, b. p. 155—160°/10 mm., D^{20} 0·9380, n_D 1·48471, $[a]_D +4·4°$.   D. F. T.

The Essential Oil of Jamaica Ginger.

FRANCIS D. DODGE (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 77—80).—The lowest-boiling fractions of oil of ginger contain an aldehyde, which may be removed as the bisulphite compound, and has now been identified with decaldehyde (compare von Soden, A., 1900, i, 605). The aldehyde has D^{15} 0·828, is optically inactive, is unstable towards alkalis, and changes spontaneously with the lapse of some years into an oil which smells like geraniol, and does not form a bisulphite compound or a semicarbazone.   J. C. W.

Essential Oil of Witch Hazel.

H. A. DICKINSON JOWETT and F. LEE PYMAN (*Pharm. J.*, 1913, **91**, 129—130).—This oil had D 0·9001, an optical rotation of +4·29° in a 100 mm. tube, was slightly soluble in 90% alcohol, and gave a small quantity of colourless precipitate when mixed with absolute alcohol. It was found to consist chiefly of a sesquiterpene having $D^{15·5}_{15·5}$ 0·8970, $a_D +14·88°$, and n_D 1·4916. A trace of a phenolic substance, a mixture of fatty acids in the free and combined state, and a mixture of solid saturated hydrocarbons were also isolated, whilst indications of the presence of other compounds, including oxygenated substances, were obtained. The oil contained 0·6% of acids (expressed as acetic acid) and 7·3% of esters (expressed as $C_{10}H_{17}·C_2H_3O_2$).   W. P. S.

Chemistry of Wood. The Resins of the Douglas Fir.

GEORGE B. FRANKFORTER and HAROLD H. BROWN (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 359).—The resin extracted from the wood of the Douglas fir yields a crystalline acid, $C_{17}H_{24}O_2$, m. p. 143·5—144·5°, which has been termed *betic acid*; its salts, and bromine and iodine compounds have been prepared.   E. G.

Oxidation of Caoutchouc.

FRANZ KIRCHHOF (*Kolloid. Zeitsch.*, 1913, **13**, 49—61).—The author has carried out experiments on the oxidation of raw and vulcanised caoutchouc by means of air at the ordinary temperature and at 100°. It is shown that on account of the unsaturated nature of the caoutchouc, an autoxidation occurs which gives rise to the formation of a relatively unstable peroxide, which then undergoes a secondary oxidation: (1) $C_{10}H_{16}+O_2 \rightarrow C_{10}H_{16}O_2$; (2) $C_{10}H_{16}+C_{10}H_{16}O_2 \rightarrow 2C_{10}H_{16}O$; (3) $C_{10}H_{16}O + O_2 \rightarrow C_{10}H_{16}O_3$. This process is accompanied, in the case of raw caoutchouc, by a softening of the material, which is quite sticky at first and later becomes hard and has a glassy nature. The latter condition is due to the presence of the higher oxidation products. The oxidation of vulcanised caoutchouc is in the same way to be regarded as a primary formation of a peroxide which then decomposes, producing the same soft and sticky substance. Further oxidation produces the hard substances and free sulphuric acid. The action of the acid appears also to consist in an oxidation of the rubber, since the acid

is reduced to sulphur dioxide. In the oxidation at 100°, a separation of water occurs; this appears to be a result of the formation of sulphuric acid, since under the same conditions raw caoutchouc does not give rise to water.

It is further shown that the combined sulphur-content after oxidation and extraction with alkali is reduced to two-thirds of the amount originally contained in the product. This and other observations lead to the conclusion that vulcanisation consists in the addition of S_8 or of a thiozone molecule to the hydrocarbon residue. Since the thiozone molecule is unstable, it is likely that vulcanised caoutchouc is a thiozonide, which probably is transformed into other products in the ageing process, and since the formation of the thiozone occurs most readily at 135—160°, the part played by the vulcanisation catalysts is to be explained by a local raising of the temperature. In the oxidation of caoutchouc by air, a notable increase in weight occurs with the formation of products soluble respectively in acetone and alkali which have an acidic character. It is also indicated that the bromide and nitrosite methods for the analysis of rubber consist of oxidation processes which are probably responsible for the untrustworthy nature of the results of these processes. J. F. S.

Synthesis of Glucosides by means of Ferments. ÉMILE BOURQUELOT (*Bull. Soc. chim.*, 1913, [iv], 13, i—xxviii).—A lecture delivered to the Chemical Society of France on May 9th, 1913.
J. F. S.

Synthetic β - Glucosides of Terpene Alcohols. III. JUHO HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1913, 53, 423—428. Compare this vol., i, 497, 639, 888).—By condensation of a-santenol and camphene hydrate with bromoacetyldextrose in the presence of silver carbonate, and the subsequent hydrolysis of the acetyl derivatives, the glucosides were obtained. *a-Santenoltetra-acetyl-d-glucoside*, $C_{26}H_{34}O_{10}$, m. p. 135·5—137° (corr.), yields on hydrolysis *a-santenol-d-glucoside*, $C_{15}H_{26}O_6$, m. p. 122·5—125·5° (corr.), $[a]_D^{20} - 44·63°$. It is readily hydrolysed by emulsin.

Camphenehydratetetra-acetyl-d-glucoside, $C_{24}H_{36}O_{11}$, m. p. 115—117° (corr.), yields on hydrolysis *camphenehydrate-d-glucoside*, $C_{15}H_{28}O_6$, m. p. 96·5—102·5° (corr.), $[a]_D^{20} - 30·56°$, which is slowly hydrolysed by emulsin. S. B. S.

Eutannin. WILHELM RICHTER (*Chem. Zentr.*, 1913, i, 1820—1821; from *Arb. Pharm. Inst. Univ. Berlin*, 9, 85—112).—Eutannin has the composition $C_{28}H_{24}O_{10}, H_2O$, $[a]_D^{15} + 58·9°$, and forms a crystalline *sodium* salt. It contains a carboxyl group and a lactone or anhydride grouping. When heated in a stream of hydrogen at 240°, a molecule of carbon dioxide is eliminated and pyrogallol sublimes. Some diphenylmethane is formed on distillation with zinc dust. *Eutannin hydrate*, $C_{28}H_{26}O_{20}$, contains two carboxyl groups owing to the opening of the lactone or anhydride ring; the *disodium* salt forms a colourless precipitate. Eutannin is hydrolysed by emulsin to gallic acid and a substance which reduces Fehling's solution on boiling. Gallic acid is similarly formed on hydrolysing with 10% sulphuric acid.

Acetyleutannin, $C_{28}H_{18}O_9(CO\cdot CH_3)_{11}$, formed on boiling with acetic anhydride, is a colourless powder composed of tiny, crystalline splinters which sinter at 180—185°, decomp. 215°.

Methyl chloro-formate acts on eutannin to form a compound
$$C_{28}H_{19}O_{11}(O\cdot CO_2Me)_6,$$
a colourless, amorphous powder, which sinters at 150—153°, decomp. 180°. Diazomethane acting on this introduces four further methyl groups, yielding a product $C_{28}H_{15}O_{10}(O\cdot CO_2Me)_5(OMe)_4,H_2O$. This is composed of small, crystalline splinters, which sinter at 125°, m. p. 137°, decomp. 179°.
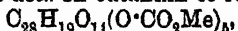
Diazomethane acting on eutannin produces at first the *methyl* derivative, $C_{28}H_{20}O_{11}(OMe)_4$, an amorphous powder, which sinters at 145°, decomp. 210—215°. On continued treatment the fully methylated compound, $C_{28}H_{13}O_{10}(OMe)_9$, is obtained, forming minute, crystalline splinters, m. p. 154—155°. On hydrolysis with sodium hydroxide, trimethylgallic acid is obtained.

The tannin obtained on hydrolysis of eutannin with sodium hydroxide has the composition $C_{14}H_{16}O_{11}$. Six hydroxyl groups in it are replaced by $-O\cdot CO_2Me$ on treatment with methyl chloro-formate. The formula $[(OH)_3(C_6H_2\cdot CO\cdot O]_2C_6H_2(CO_2H)\cdot O\cdot C_6H_4O(CO)(OH)_4$ is proposed for eutannin.   E. F. A.

Arsenites of Alkaloids. ALFRED C. MANGOLD (*Eighth Inter. Cong. App. Chem.*, 1912, **17**, 37—43).

—Analyses of compounds of arsenious acid with various alkaloids showed that the acid does not form true salts with quinine, cinchonidine, cinchonine, quinidine, brucine, and strychnine ; the compounds obtained under varying conditions of preparation were mixtures of arsenious acid with the alkaloids. Arsenic acid, however, forms well-crystallised, definite salts with these alkaloids.   W. P. S.

Occurrence of Histidine-betaine in Fungi. ERNST WINTER-STEIN and CAMILLE REUTER (*Zeitsch. physiol. Chem.*, 1913, **86**, 234—237).

—The base $C_9H_{15}O_2N_3$ obtained by Reuter (A., 1912, ii, 593) from fungi is shown to be histidine-betaine identical with that obtained by Barger and Ewins (this vol., i, 529) from ergothionin and the synthetic product made by Engeland and Kutscher (*ibid.*). The monopicrate, m. p. 201°, forms slender, soft needles. The dipicrate, $2H_2O$, loses this water at 105°, and forms flat, thin prisms, or long plates, m. p. 212—213°. The base has $[a]_D +41\cdot1°$.

E. F. A.

Some Derivatives of 8-Hydroxyquinoline. HANS SCHULLER (*J. pr. Chem.*, 1913, [ii], **88**, 180—188).

—8 : 8'-*Dihydroxy-5 : 5'-diquinolylmethane*, $CH_2(C_9H_5N\cdot OH)_2$, obtained in the form of its *sulphate* (stellar aggregates of yellow needles, m. p. 198—200°) by the addition of 40% aqueous formaldehyde to a well cooled solution of 8-hydroxyquinoline in sulphuric acid, is precipitated from its salts by aqueous ammonia as a white, amorphous precipitate (decomp. 247°), which separates from pyridine in hexagonal crystals and couples with diazotised *m*-toluidine and *α*-naphthylamine, yielding carmine-red and reddish-brown *azo-dyes*. The *hydrochloride*, B,2HCl, crystallises in

radiating clusters of lustrous, silky needles (decomp. 260°); the *zinci-chloride* forms yellowish-green, prismatic crystals; the *diacetyl* derivative has m p. 160°, and decomposes slowly on exposure to air; the *dibenzoyl* derivative, prepared by the pyridine method, separates from alcohol in small crystals, and has an odour resembling that of ethyl benzoate.

7 : 7'-*Dinitroso*-8 : 8'-*dihydroxy*-5 : 5'-*diquinolylmethane* (or 7 : 7'-*di-oximino*-8 : 8'-*diketo*-5 : 5'-*di*-7 : 8-*dihydroquinolylmethane*),

$$CH_2[C_9H_4N(NO)\cdot OH]_2,$$
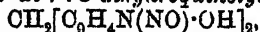
or $CH_2(C_9H_4ON:N\cdot OH)_2$, prepared by the addition of sodium nitrite to an aqueous solution of the sulphate or hydrochloride, is a yellow crystalline substance, which explodes at about 130°, and is precipitated from its solution in sodium carbonate by acetic acid in a red, gelatinous condition. With salts of iron, nickel, copper, and many other metals, it yields coloured precipitates, which are more or less soluble in mineral acids, but insoluble in dilute acetic acid. Unsuccessful attempts to condense 8 hydroxyquinoline with oxalic acid, formic acid, and carbon tetrachloride are also recorded.   F. B.

The Desmotropy of *o*- and *p*-Quinonoid Salts in the Thiazine Group. RUDOLF PUMMERER and SEBASTIAN GASSNER (*Ber.*, 1913, **46**, 2310—2327).—In order to throw further light on the debated constitution of the thiazines, the authors have turned their attention to some of the simpler salts and have examined them chemically and optically; they find in certain cases an equilibrium between the ortho- and para-constitutions favoured by Kehrmann and Hantzsch respectively.

Their results with the phenazothionium salts differ in several respects from those of Kehrmann and Veselý (A., 1902, i, 186). The action of bromine on an alcoholic solution of thiodiphenylamine at even −15° yielded a *dibromide*, $NHBr\!<\!\!{}^{C_6H_4}_{C_6H_4}\!\!>\!SBr$, prisms, which readily decomposes with liberation of hydrogen bromide; it is reconverted by sulphurous acid into thiodiphenylamine. The *dichloride* is still less stable, but the more stable *di-iodide*, blackish-brown crystals, can be obtained by double decomposition of the dibromide and potassium iodide and also by the action of iodine on thiodiphenylamine in chloroform solution. Treatment of an acetone solution of the di-iodide with sodium acetate causes the production of a salt derived probably from a bimolecular colourless *base*.

The ferrochloride described earlier, from its quantitative reduction with stannous chloride, appears to be a *meri*-quinonoid compound which readily accounts for the deposition of thiodiphenylamine when its solution in hydrochloric acid is diluted. *Phenazothionium perchlorate,* obtained by the action of perchloric acid on diphenylaminesulphoxide (Barnett and Smiles, T., 1910, **97**, 186), is a stable, crystalline substance, which, like the phenazothionium salts generally, shows in dilute hydrochloric acid an absorption band in the green portion of the spectrum; a green *diperchlorate* was also obtained. In addition to the green picrate obtained by Kehrmann and Veselý, the authors have isolated the unstable brown intermediate product, which proves to

be of the same composition, the green picrate being regarded as a polymeride of the brown; a very dilute solution of the green picrate in nitrobenzene turns brown, the change in colour being favoured by warming and dilution, whilst stronger solutions of both forms at first have the characteristic colour of the respective solids, but shortly assume an intermediate tone.

Phenazothione (for which the authors prefer the term thiazone), obtained by a slight modification of Kehrmann's method, judging from its absorption spectrum and its reaction with magnesium phenyl bromide, can hardly have the suggested phenol-betaine structure :

$$N\!\!<^{C_6H_4}_{C_6H_3\!-\!O}\!\!>\!S.$$
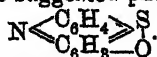
This view is confirmed by the behaviour of its *hydrochloride*, which exists in two forms. On intimately mixing the base with hydrochloric acid a brown solution is obtained which changes to violet and subsequently deposits violet needles; the violet hydrochloride can be obtained directly by reaction in benzene-ether solution. The conversion of the brown form into the violet could be followed photometrically, and it was found that a unimolecular reaction occurs, yielding an equilibrium mixture, and that the velocity is independent of the concentration; from these facts the change must be an isomerisation, probably of the brown para-quinonoid salt, $N\!\!<^{C_6H_3O(HCl)}_{C_6H_4}\!\!>\!S$, into violet

ortho-quinonoid, $N\!\!<^{C_6H_3(OH)}_{C_6H_4}\!\!>\!SCl$; reduction of the brown salt (which was only obtained in solution) was usually accompanied by more or less isomerisation to the violet salt, which is less easily reduced. Only one *hydriodide* was obtainable, and from its brown colour it is probably of the para-quinonoid structure. Similar phenomena are met with 3-*methoxythiodiphenylamine*, leaflets, m. p. 163°, which on oxidation by p-benzoquinone in acetic acid containing a little sulphuric acid gives a mixture of ortho- and para-quinonoid salts; addition of perchloric acid causes precipitation of the o-quinonoid violet *perchlorate*, which in the absence of any excess of acid gives a brown solution in water, but on addition of a few drops of acid the violet form is obtained. With 3-*benzoyloxythiodiphenylamine*, leaflets, m. p. 202—203°, obtained like the corresponding methoxy-compound by acting on a reduced solution of phenazothione, only ortho-quinonoid salt formation could be observed.

The acetylated amino-compounds, such as diacetylthionine (free *base*, needles, decomp. above 250°), are only ortho-quinonoid, whilst from similar colour considerations aminophenazothionium hydrochloride is of para-quinonoid constitution, but shows desmotropy analogous to that of phenazothione hydrochloride, and is transformed by concentrated acid into a brown ortho-quinonoid salt. Indications of such structural change could also be detected with thionine, but not with methylene-blue.   D. F. T.

The Deepening of Colour by Auxochrome Groups and Colours of an Higher Order. FRITZ STRAUS and A. ZELME (*Ber.*, 1913, 46, 2267—2283).—From a study of the *meri*-quinonoid salts of

the *p*-phenylenediamine and benzidine series, Piccard (this vol., i, 895) has drawn the conclusion that Nietzki's rule, concerning the deepening of the colour from yellow to green by auxochrome groups, requires extension so as to include colours of a higher order. When the auxochromic effect has been gradually increased by substitution so that the colour has successively passed from yellow to red, blue and green, further increase in the auxochrome action is accompanied by a repetition of the colours in the same order; the colours of the second series are said to be of the second order.

The authors have arrived at the same conclusion from a consideration of the relationship of the yellow auramine to the blue and green dyes of the diaminodiphenyl and diaminotriphenyl series previously described by Straus and Bormann (A., 1910, i, 281). The latter dyes are derived from the reddish-blue salts of tetramethyldiaminobenzhydrol, $NMe_2 \cdot C_6H_4 \cdot CH:C_6H_4:NMe_2Cl$ (I), by replacement of the central methane hydrogen by chlorine, cyanogen, phenyl and other groups.

The yellow auramine and the orange-yellow salts of Michler's ketone differ from the above dyes in that the chromophoric groups are replaced by the auxochromic, hydroxyl and amino-groups, which thus cause a change in colour from blue to yellow; the yellow colour of the auramine is, therefore, considered to be of the second order.

This view is supported by the observation of Semper (A., 1911, i, 577), that the acetylated auramine base yields reddish-blue salts, $NMe_2 \cdot C_6H_4 \cdot C(NHAc):C_6H_4:NMe_2Cl$; the auxochromic effect of the amino-group almost completely disappears on acetylation, so that the yellow colour of the second order of the auramine passes back again into the blue colour of the first order shown by the parent substance (I).

The conception of colours of a higher order also throws light on the relationships existing between the dyes of the diamino- and triamino-triphenyl series. The dyes of the triamino-series are not so deep in colour as those of the diamino-series, although they are produced from the latter by the introduction of the auxochrome amino-group. Thus, the red magenta corresponds with Döbner's violet, and the reddish-violet tetramethylmagenta with malachite-green. On the other hand, if the effect of the third amino-group in the magenta series is caused to disappear by acetylation, or by the conversion of the nitrogen atom into the quinquevalent condition, the colour apparently deepens. These anomalies disappear if it is assumed that the colours of the triaminotriphenyl series are of the second order, and those of the malachite-green group of the first order.

The authors also point out that whilst nitrosobenzene in the unimolecular condition is bluish-green and *p*-nitrosodimethylaniline pure green, the colour of *p*-nitrosodiphenylamine is yellow, and that tetramethyldiaminothiobenzophenone is orange-red, whilst thiobenzo-phenone is blue; from this the conclusion is drawn that the colours of *p*-nitrosodiphenylamine and tetramethyldiaminothiobenzophenone are of the second order.

Attempts have been made to prepare dyes having colours of the second order by replacing the *p*-hydrogen atoms of the terminal phenyl groups in viridine, $C_6H_5 \cdot NH \cdot C_6H_4 \cdot CPh:C_6H_4:NHCl \cdot C_6H_5$, by chlorine,

bromine, methyl, methoxy- and ethoxy-groups. The attempts, however, were not successful, the various substituents producing very little change in the colour of the parent substance ; even replacement of the terminal phenyl groups by the naphthyl or diphenylyl groups failed to produce the desired effect.

The substituted viridines were all prepared by fusing di-*p*-methoxy-triphenylcarbinol with the necessary substituted aniline (3 to 4 mols.) and benzoic acid (3 mols.) at 120—160° and isolated in the form of their chlorides.

The corresponding imine bases,

$$X \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot CPh : C_6H_4 : N \cdot C_6H_4 X,$$
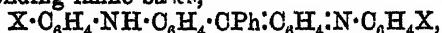
crystallise with benzene in dark reddish-brown needles having a green glance, and appear to polymerise when kept. The carbinols were prepared by dissolving the picrates or chlorides in pyridine and allowing the solution, after dilution with benzene or ether, to flow slowly into dilute aqueous alkali ; only in a few cases could the carbinols be obtained crystalline. Ethers of the carbinols were also prepared, and resemble the latter in being difficult to obtain in the crystalline condition.

The *chloride* of *di-p-methylviridine*, prepared from *p*-toluidine, separates from acetone in small, lustrous, bronze crystals of the composition $C_{33}H_{29}N_2Cl, C_3H_6O$ (decomp. 248—250°) ; it crystallises with alcohol in needles having a green metallic glance. The *picrate* forms dark green needles, m. p. 211°, with previous sintering at 205° ; the *imine base* has m. p. 182°.

The *chloride* of *di-p-chloroviridine*, prepared from *p*-chloroaniline, forms lustrous, metallic green needles, m. p. about 285°, the *picrate*, prismatic crystals, having a golden-yellow or green metallic lustre, m. p. 243°, with previous sintering at 236° ; the *imine base* crystallises in dark brown needles, m. p. 136°, when rapidly heated.

The *chloride* of *di-o-chloroviridine* has m. p. 191° ; the *picrate* crystallises in leaflets of a coppery-red, metallic lustre, m. p. 148° ; the *imine base* has m. p. 107°.

The *chloride* of *di-p-bromoviridine* forms a powder having a bronze lustre, m. p. indefinite (290—305°) ; the *picrate* crystallises from acetone in prismatic crystals of a golden-yellow, metallic glance, m. p. 253—257° ; the *imine base* has m. p. 186—187°.

The *chloride* of *di-p-methoxyviridine* forms green, metallic, lustrous needles ; the *picrate* forms green or golden-bronze, lustrous crystals, m. p. 205—208° ; the *imine base*, m. p. 167°, crystallises with benzene (1 mol.).

The *chloride* of *di-p-ethoxyviridine* has m. p. 243—245° ; the *picrate* separates from acetone in light green, metallic, lustrous crystals, which on drying pass into a lustrous coppery modification, m. p. 176° ; the *imine base* crystallises with benzene (1 mol.), m. p. 97°.

The following derivatives of *di-p-nitroviridine* were prepared : the *chloride* ; *picrate*, lustrous, bronze crystals ; *imine base*, dark brown needles, m. p. 176—178° ; the *carbinol*, which sinters and decomposes at 110—115°, and is completely fused at 140° ; the *ethyl ether*, which is light yellow, becomes brown at 200°, and has m. p. 204°.

The *chloride* of *di-p-phenylviridine*, prepared from *p*-aminodiphenyl,

forms a dark green, metallic,' lustrous powder, m. p. 300—305°; the *picrate*, dark red scales, m. p. 252°, with previous sintering at 247°; the *imine base* crystallises with benzene (1 mol.), and has m. p. 136°; the *carbinol*, a light pink powder, and *ethyl ether* were also prepared.

β-Naphthylaminofuchsone-β-naphthylimine,

$$C_{10}H_7\cdot NH\cdot C_6H_4\cdot CPh:C_6H_4:N\cdot C_{10}H_7,$$
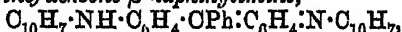
prepared from β-naphthylamine, has m. p. 147°; the *chloride* crystallises from acetone in brown needles of a bronze lustre, m. p. 290—300° (decomp.); the *picrate* in cubical crystals, sintering at 215°, m. p. 224°; the *carbinol* and *leuco*-compound do not crystallise.

F. B.

Ring Closing Accompanied by the Elimination of a Nitrogroup from the Benzene Nucleus. SIEGMUND REICH and GEORGES GAIGAILIAN (*Ber.*, 1913, 46, 2380—2386).—When potassium hydroxide is added to 2 : 6-dinitrobenzaldehydephenylhydrazone, the red alcoholic solution becomes deep blue, but in a few minutes the colour lessens and changes to a pale yellow; pale yellow needles, m. p. 165°, crystallise out. The change is analogous to that observed by V. Meyer with the phenylhydrazone of methyl dinitrophenylglyoxylate (compare A., 1889, 516).

The blue colour is due to the formation of the potassium salt, $C_6H_3(NO_2)_2\cdot CH:N\cdot NPhK$, from which potassium nitrite is eliminated, and 7-nitro-1-phenylisoindazole is formed, $NO_2\cdot C_6H_3\overset{CH}{\underset{NPh}{>}}N$.

Corresponding *iso*indazole derivatives are formed by the substituted phenylhydrazones, or by the naphthyl- or benzyl-hydrazones. The semicarbazone does not react in this manner.

When the imide hydrogen atom is replaced there is no reaction; thus neither the phenylmethyl- nor the phenylbenzyl-hydrazones shows the reaction.

The *iso*indazole derivatives crystallise well, and are stable compounds. The presence of the phenyl and nitro-groups reduces the basic properties, so that the hydrochlorides are not precipitated on passing hydrogen chloride into the ethereal solution of the base. They are especially resistant towards reducing agents.

7-*Nitro*-1-*phenyl*isoindazole crystallises in yellow needles, m. p. 165°.

2 : 6-*Dinitrobenzaldehyde*-p-*bromophenylhydrazone* forms red crystals, m. p. 176° (blackening). The corresponding 7-*nitro*-1-p-*bromophenyl*-isoindazole separates in yellow crystals, m. p. 185° (blackening).

2 : 6-*Dinitrobenzaldehyde* - p - *nitrophenylhydrazone* forms reddishbrown crystals, m. p. 207—208°. The isomeric o-*nitrophenylhydrazone* gives similar-coloured crystals, m. p. 220—221°.

7-*Nitro*-1-p-*nitrophenyl*isoindazole yields yellow, microscopic crystals, m. p. 261°.

7-*Nitro*-1-o-*nitrophenyl*isoindazole forms yellow needles, m. p. 162—163°.

2 : 6-*Dinitrobenzaldehyde*-a-*naphthylhydrazone* forms red crystals, m. p. 205—206°.

7-*Nitro*-1-a-*naphthyl*isoindazole gives yellow crystals, m. p. 113—114°.

The isomeric *β naphthylhydrazone* crystallises in tiny red needles, m. p. 183—184°, whilst the 7-*nitro*-1-*β naphthyl*isoindazole separates in yellow crystals, m. p. 152—153°.

2 : 6-*Dinitrobenzaldehydebenzylhydrazone* crystallises in citron-yellow needles, m. p. 86°.

7-*Nitro*-1-*benzyl*isoindazole forms tiny, pale yellow, lustrous needles, m. p. 97—98°.

2 : 6-*Dinitrobenzaldehydephenylmethylhydrazone* separates in reddish-yellow crystals, m. p. 127°.

2 : 6-*Dinitrobenzaldehydephenylbenzylhydrazone* crystallises in yellow needles, m. p. 110°.

2 : 6-*Dinitrobenzaldehydesemicarbazone* forms a yellow, crystalline powder, m. p. 207—208°.

2 : 6 : 2′ : 6′-*Tetranitrobenzylideneazine*,

$$C_6H_3(NO_2)_2 \cdot CH{:}N \cdot N{:}CH \cdot C_6H_3(NO_2)_2,$$
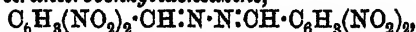
prepared by the interaction of hydrazine hydrochloride with the aldehyde, forms pale yellow-coloured needles, m. p. 246—247°.

E. F. A.

Bisdiphenyleneacetylhydrazide Chloride and its Reaction Products. ROBERT STOLLÉ, H. MUNZEL, and F. WOLF (*Ber.*, 1913, 46, 2339—2352).—The elimination of halogen or of halogen hydracid at the 1 : 6-position occurs with bisdiphenyleneacetylhydrazide chloride just as with bisdiphenylacetylhydrazide chloride (Stollé and Laux, A., 1911, i, 508; Stollé and Schmidt, A., 1912, i, 980, 1035). Corresponding with the greater mobility of the *α*-hydrogen atom of diphenyleneacetic acid it is found that derivatives such as bisdiphenyleneacetylhydrazide chloride readily undergo oxidation to azo-compounds, whilst others can be further oxidised to tetrazine derivatives (compare Wislicenus and Russ, A., 1910, i, 840).

Diphenyleneacetylhydrazide, $CH(C_6H_4)_2 \cdot CH \cdot CO \cdot NH \cdot NH_2$, needles, m. p. above 360° (decomp.), was obtained by heating ethyl diphenyleneacetate with a sesquimolecular proportion of hydrazine hydrate at 120° for three hours; its *hydrochloride,* lustrous scales, is precipitated from solution by concentrated hydrochloric acid; *benzylidene* derivative, needles which sinter near 250°; *acetone* condensation product, lustrous needles, m. p. near 200° if rapidly heated.

If diphenyleneacetylhydrazide is heated for two hours with ethyl diphenyleneacetate in molecular proportion at 250°, symmetrical *bisdiphenyleneacetylhydrazide,* $CH(C_6H_4)_2 \cdot CO \cdot NH \cdot NH \cdot CO \cdot CH(C_6H_4)_2$, needles, m. p. 340°, from nitrobenzene, is obtained, and it can also be produced by the interaction of equimolecular proportions of diphenyleneacetyl chloride and hydrazine hydrate in cooled ethereal solution. When treated in suspension in benzene or carbon tetrachloride with phosphorus pentachloride at water-bath temperature, this symmetrical hydrazide is converted into *bisdiphenyleneacetylhydrazide chloride,* $CH(C_6H_4)_2 \cdot CCl{:}N \cdot N{:}CCl \cdot CH(C_6H_4)_2$, colourless crystals, which at its m. p. (approximately 192°) or in solution in boiling xylene or nitrobenzene assumes a deep red colour, due doubtless to elimination of hydrogen atoms at the 1 : 6-positions by oxidation with formation of the *azo*-compound, $C(C_6H_4)_2{:}CCl \cdot N{:}N \cdot CCl{:}C(C_6H_4)_2$. The hydrazide

chloride, when treated in benzene solution with an alcoholic solution of sodium ethoxide or with ammonia, or such bases as mercuric oxide and lead oxide, loses a molecule of hydrogen chloride, producing *bisdiphenylenesuccinonitrile*, a colourless, crystalline powder, m. p. 242°. If in the reaction with sodium ethoxide the solution of the latter is a concentrated one and the reaction mixture is heated, the nitrile undergoes further hydrolysis with scission of carbon dioxide, yielding bisdiphenylene-ethane. By boiling with acetic acid and zinc dust the nitrile undergoes successive reduction and hydrolysis to diphenyleneacetamide, m. p. 251°.

If an intimate mixture of bisdiphenyleneacetylhydrazide chloride and phosphorus pentachloride is heated for an hour at 180—200°, *bischlorodiphenyleneacetylhydrazide chloride*,

$$CCl(C_6H_4)_2 \cdot CCl \colon N \cdot N \colon CCl \cdot CCl(C_6H_4)_2,$$
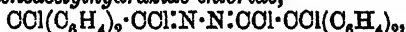
pale red crystals, m. p. 240°, with reddening, is obtained. When heated in high-boiling solvents, a deep red colour develops, due to elimination of chlorine and formation of *bischlorodiphenylenevinyldi-imide*,

$$C(C_6H_4)_2 \colon CCl \cdot N \colon N \cdot CCl \colon C(C_6H_4)_2,$$
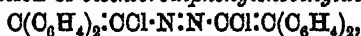
almost black, lustrous needles, m. p 295°, which is best produced by the action of mercury on the bischlorodiphenyleneacetylhydrazide chloride in benzene solution; the di-imide can unite with chlorine regenerating its parent substance, and is further reduced in benzene solution by hydrazine hydrate, yielding 3 : 6-difluorenyldihydrotetrazine,

$$CH(C_6H_4)_2 \cdot C \underset{NH \cdot NH}{\overset{N——N}{<} {>}} C \cdot CH(C_6H_4)_2,$$ m. p. 290°, and by acetic acid

and zinc dust to iminomethylfluorene, m. p. 148—149° (compare Wislicenus and Russ, *loc. cit.*). The addition of bromine to bischlorodiphenylenevinyldi-imide, effected in benzene solution, yields *bisbromodiphenyleneacetylhydrazide chloride*,

$$CBr(C_6H_4)_2 \cdot CCl \colon N \cdot N \colon CCl \cdot CBr(C_6H_4)_2,$$
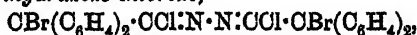
colourless crystals, m. p. 245°, which like the corresponding chloro-compound readily passes into the red azo-compound at its m. p. or when heated in high-boiling solvents. On treatment of the di-imide compound in benzene solution with amyl nitrite and acetic acid, the colour disappears and *a-nitroso-a'-hydroxy-aa'-bisdiphenyleneacetylhydrazide chloride*, $OH \cdot C(C_6H_4)_2 \cdot CCl \colon N \cdot N \colon CCl \cdot C(C_6H_4)_2 \cdot NO$, colourless, microscopic needles, m. p. near 145°, with reddening, is formed.

When bisdiphenyleneacetylhydrazide chloride is heated for several days in benzene solution with phosphoryl chloride and phosphoric oxide, *bisfluorenyl-1 : 3 : 4-oxadiazole*,

$$CH(C_6H_4)_2 \cdot C \underset{-O}{\overset{N \cdot N}{<} {>}} C \cdot CH(C_6H_4)_2,$$
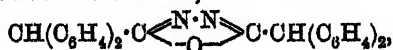
colourless needles, m. p. 223°, is obtained ; this assumes a blue coloration at its m. p. or when heated in high-boiling solvents ; by heating in benzene solution with phosphorus pentachloride for several hours it is converted into 2 : 5-*bischlorodiphenylenemethyl-1 : 3 : 4-oxadiazole*,

$$C(C_6H_4)_2Cl \cdot C \underset{-O}{\overset{N \cdot N}{<} {>}} CCl(C_6H_4)_2,$$ colourless prisms, m. p. 227°, which

can also be obtained by the action of thionyl chloride on s-diphenyleneacetylhydrazide. This product when heated in high-boiling solvents, or

preferably when shaken in benzene solution with mercury, loses chlorine with formation of blue 2 : 5-*bisdiphenylenemethylenedihydro*-1 : 3 : 4-*oxadiazole*, $C(C_6H_4)_2 \cdot C <^{N:N}_{O}> C:C(C_6H_4)_2$, m. p. above 360°, and when boiled in alcoholic solution for several days undergoes conversion into 2 : 5-*bisethoxydiphenylenemethyl*-1 : 3 : 4-*oxadiazole*,

$$OEt \cdot C(C_6H_4)_2 \cdot C <^{N \cdot N}_{O} > C \cdot C(C_6H_4)_2 \cdot OEt,$$
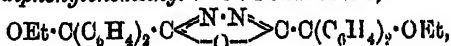
a colourless, crystalline powder, m. p. 290° (decomp.).

Bisdiphenyleneacetylhydrazide chloride, when heated under reflux for five hours with an equal quantity of hydrazine hydrate, condenses with the latter, producing 3 : 6-*difluorenyldihydrotetrazine*,

$$CH(C_6H_4)_2 \cdot C <^{N-----N}_{NH \cdot NH} > CH(C_6H_4)_2,$$
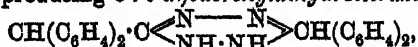
a colourless powder, m. p. 290°, together with 1-*amino*-2 : 5-*difluorenyl*-1 : 3 : 4-*triazole*, $CH(C_6H_4)_2 \cdot C <^{N-----N}_{N(NH_2)} > C \cdot CH(C_6H_4)_2$, microscopic tablets, m. p. 285°, which is also obtained by the action of hot alcoholic hydrogen chloride on the former product. The latter substance when treated in cold alcoholic solution with hydrogen chloride and sodium nitrite undergoes conversion into 2 : 5-*difluorenyl*-1 : 3 : 4-*triazole*, $CH(C_6H_4)_2 \cdot C <^{N \cdot N}_{NH} > C \cdot CH(C_6H_4)_2$, needles, m. p. 217°. The interaction of bisdiphenylacetylhydrazide chloride and aniline at 150° gives rise to 1-*phenyl*-2 : 5-*difluorenyl*-1 : 3 : 4-*triazole*,

$$CH(C_6H_4)_2 \cdot C <^{N \cdot N}_{NPh} > C \cdot CH(C_6H_4)_2,$$
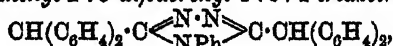
a pale yellow, crystalline powder, m. p. 270°, the course of the reaction being strikingly different from that with ammonia (see above). The last product, in suspension in carbon tetrachloride and exposed to the rays from a quartz lamp, is converted by chlorine into 1-*dichlorophenyl*-2 : 5-*bisdiphenylenechloromethyl*-1 : 3 : 4-*triazole*,

$$CCl(C_6H_4)_2 \cdot C <^{N-----N}_{N(C_6H_3Cl_2)} > C \cdot Cl(C_6H_4)_2,$$
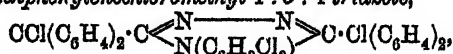
a colourless powder, m. p. above 360°, the solution of which in molten naphthalene becomes blue on shaking with mercury, probably due to the formation of unstable 1-*dichlorophenyl*-2 : 5-*bisdiphenylenemethylene*-2 : 5-*dihydro*-1 : 3 : 4-*triazole*, $C(C_6H_4)_2 : C <^{N=====N}_{N(C_6H_3Cl_2)} > C:C(C_6H_4)_2$.

When shaken in benzene suspension with amyl nitrite, 3 : 6-difluorenyldihydrotetrazine becomes oxidised to 3 : 6-*difluorenyltetrazine*, $CH(C_6H_4)_2 \cdot C <^{N-N}_{N=N} > C \cdot CH(C_6H_4)_2$, red needles, m. p. 225° (decomp.), the reverse change being possible by reduction with zinc dust and acetic acid. 3 : 6-Difluorenyltetrazine when subjected to the action of chlorine in boiling carbon tetrachloride under the influence of rays from a quartz lamp gives 3 : 6-*bischlorodiphenylenemethyltetrazine*, $CCl(C_6H_4)_2 \cdot C <^{N-N}_{N=N} > C(C_6H_4)_2Cl$, violet-black needles, m. p. 206° (decomp.), as a substitution product. Although already formed 3 : 6-

difluorenyltetrazine is not further oxidisable by amyl nitrite, if 3 : 6-difluorenyldihydrotetrazine is heated in benzene solution with amyl nitrite, the oxidation passes this stage, yielding 3 : 6-*bisdiphenylene-methylenedihydrotetrazine*, $C(C_6H_4)_2{:}C{<}^{N=N}_{N=N}{>}C{:}C(C_6H_4)_2$, green prisms, m. p. 240° (decomp.), which is also obtainable by the action of mercury on a benzene solution of 3 : 6-bischlorodiphenylene-methyltetrazine or 3 : 6-bisbromodiphenylenemethyltetrazine, into which substances it can be reconverted by the action of the respective halogens. When heated alone to 240°, 3 : 6-bisdiphenylenemethylene-dihydrotetrazine loses half its total nitrogen, and passes into bis-diphenylenesuccinonitrile ; by the action of bromine in benzene solution it is quantitatively converted into 3 : 6-*bisbromodiphenylenemethyl-tetrazine*, $CBr(C_6H_4)_2{\cdot}C{<}^{N=N}_{N=N}{>}C{\cdot}CBr(C_6H_4)_2$, a reddish-violet powder, decomp. near 260°, from which the bromine is removable by the action of mercury on its benzene solution. The action of sodium ethoxide on the bromine compound failed to yield any corresponding ethoxy-derivative, the only product being bisdiphenylene-ethane.

D. F. T.

Preparation and Reactions of 2 : 4-Dichlorophenylhydrazono-pyruvyl Chloride. CARL BÜLOW and PETER NEBER (*Ber.*, 1913, **46**, 2370—2379. Compare Bülow and Neber, this vol., i, 207).—On hydrolysing ethyl anilinoacetoacetate to the free carboxylic acid and allowing chlorine to act on this in alcoholic solution, 2 : 4-*dichloro-phenylhydrazonopyruvyl chloride* is obtained,

$$CH_3{\cdot}CO{\cdot}CCl{:}N{\cdot}NH{\cdot}C_6H_3Cl_2,$$
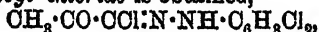
whereas carbon dioxide and hydrogen chloride are liberated. The chloride is very reactive ; on treatment with ammonia or hydrazine, action can be controlled, so that only the chlorine and not the keto-group is replaced by the amino- or hydrazino-group with the formation of the basic compounds, (A) 2 :4-*dichlorophenylhydrazonopyruvamide*, $CH_3{\cdot}CO{\cdot}C(NH_2){:}N{\cdot}NH{\cdot}C_6H_3Cl_2$, and (B) 2 : 4-*dichlorophenylhydrazono-pyruvylhydrazide*, $CH_3{\cdot}CO{\cdot}C{<}^{NH\cdot NH_2}_{N\cdot NH\cdot C_6H_3Cl_2}$.

When phenylhydrazine acts on the aminohydrazone (A), the colour-less basic osazone having the constitution

$$NHPh{\cdot}N{:}CMe{\cdot}C(NH_2){:}N{\cdot}NH{\cdot}C_6H_3Cl_2,$$
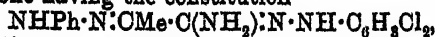
which is sensitive to light, is formed. The Bordeaux-red solution in concentrated sulphuric acid is turned blue both by oxidising agents and by atmospheric oxygen with the formation of osotetrazone.

The same osazone is obtainable from 2 : 4-dichlorophenylhydrazono-pyruvyl chloride and phenylhydrazine, which condense to the *phenylhydrazone* of the chloride, $\begin{array}{l}\alpha \quad CCl{:}N{\cdot}NH{\cdot}C_6H_3Cl_2\\ \beta \quad CH_3{\cdot}C{:}N{\cdot}NHPh\end{array}$. This is converted by alcoholic acid into the corresponding α-amino-osazone, The *hydrazone* of 2 : 4-dichlorophenylhydrazonopyruvamide,

$$NH_2{\cdot}C({:}N{\cdot}NH{\cdot}C_6H_3Cl_2){\cdot}CMe{:}N{\cdot}NH_2,$$

3 x 2
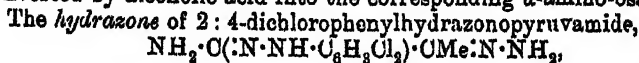
is typical of another class of compounds belonging to the basic osazonoid series; it no longer dissolves with a characteristic coloration in concentrated sulphuric acid, and cannot be oxidised to osotetrazone. The corresponding *hydrazide* behaves similarly.

2 : 4-*Dichlorophenylhydrazonopyruvyl chloride* crystallises in snowwhite needles, m. p. 125°, dissolving in concentrated sulphuric acid with a pure yellow coloration. With pyridine on boiling or on prolonged contact in the cold it forms a *compound* crystallising in red needles, m. p. 168°. The corresponding *amide* crystallises in centimetre-long, faintly yellow needles, m. p. 193°, and dissolves in concentrated sulphuric acid with a faint yellow coloration.

The *phenylhydrazone* of 2 : 4-*dichlorophenylhydrazonopyruvamide* separates in bunches of snow-white needles, m. p. 149° (decomp.).

The *phenylhydrazone* of the corresponding *chloride* is deposited in large, straw-yellow needles from chloroform or fine matted needles from acetic acid, m. p. 208° (decomp.), giving a brownish-yellow solution in concentrated sulphuric acid.

The *hydrazone* of 2 : 4-*dichlorophenylhydrazonopyruvamide* crystallises in large, colourless needles becoming yellow on exposure; it sinters at 120°, m. p. 130°. The corresponding *acetylhydrazone* forms colourless crystals, m. p. 217°.

2 : 4-*Dichlorophenylhydrazonopyruvylhydrazide* forms pale yellow needles, m. p. 131°. It is remarkably electric. It dissolves in concentrated sulphuric acid with a yellowish-brown coloration which deepens on keeping. The corresponding *acetylhydrazide* crystallises in colourless needles which sinter at 150°, m. p. 199°; they become yellow on exposure.   E. F. A.

Purines. XI. 2 : 8 - Dioxy-6-methyl - 9 - ethylpurine. CARL O. JOHNS and EMIL J. BAUMANN (*J. Biol. Chem.*, 1913, 15, 119—125).—The preparation of a derivative of 9-ethylpurine is described. 6-Chloro-2-ethylthiol-4-methylpyrimidine,

$$SEt \cdot C \underset{N \cdot CMe}{\overset{N=CCl}{<}} CH,$$
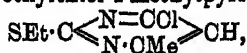
was heated with aqueous ethylamine, and gave an excellent yield of 6-*ethylamino-2-ethylthiol-4-methylpyrimidine*,

$$SEt \cdot C \underset{N----CMe}{\overset{N:C(NHEt)}{<}} CH,$$
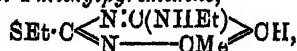
colourless, pointed prisms, m. p. 70°. Boiling with hydrochloric acid converted this into 6-*ethylamino-4-methyl-2 : 3-dihydro-2-pyrimidone*,

$$CO \underset{NH----CMe}{\overset{N:C(NHEt)}{<}} CH,$$ acicular prisms, m. p. 245—250° (decomp.)
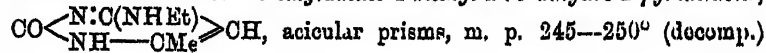
(*hydrochloride*, colourless, diamond-shaped plates, m. p. 214—215°); this gave 5-*nitro-6-ethylamino-4-methyl - 2 : 3 - dihydro - 2 - pyrimidone*, colourless needles, decomp. 238°, charring at 260—265°, which was very readily reduced by means of freshly precipitated ferrous hydroxide to 5-*amino-6-ethylamino 4-methyl-2 : 3-dihydro-2-pyrimidone*,

$$CO \underset{NH----CMe}{\overset{N:C(NHEt)}{<}} C \cdot NH_2,$$ clusters of needles. Heating with carbamide converted this into the desired 2 : 8-*dioxy-6-methyl-9-ethylpurine*,

$$CO\diagdown^{N:CMe}_{NH-C}\diagup^{C-NH}_{NEt\cdot CO}$$, which crystallises in sheaves of needles like

tyrosine; it has a pearly lustre, and does not melt at 310°.

<div align="right">E. F. A.</div>

Etherification of o-Hydroxyazo-compounds. III. G CHARRIER and G. FERRERI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 854—872. Compare A., 1912, i, 812; this vol., i, 535).—In the present paper are described nitrates of azo-2-naphthyl ethers. They are obtained by adding an ethereal solution of nitric acid to ethereal solutions of the ethers. They are more stable than the corresponding hydrochlorides (*loc. cit.*), and have a definite m. p., but on cooling after fusion an equimolecular mixture of the corresponding 1-nitro-2-naphthyl ether and the diazonium nitrate is found to have been formed. The constitution of these nitrates is probably that represented by the

formula: $C_{10}H_6\diagdown^{N:NHAr(ONO_2)}_{OHR(ONO_2)}$.

The nitrate of 1-benzeneazo-2-naphthyl methyl ether, m. p. 67°, has already been described (*loc. cit.*), as has also the corresponding ethyl ether derivative, m. p. 80—81°.

1 o-*Tolueneazo-2-naphthyl methyl ether hydrochloride*,

<div align="center">$C_{18}H_{16}ON_2,2HCl$,</div>

forms metallic green needles; the *nitrate*, $C_{18}H_{16}ON_2,2HNO_3$, forms large, green, acicular crystals, m. p. 71° (decomp.). The *nitrate* of the ethyl ether, $C_{19}H_{18}ON_2,2HNO_3$, crystallises in cantharides-green laminæ, m. p. 62—63° (decomp.).

The *nitrate* of 1-m-*tolueneazo-2-naphthyl methyl ether*,

<div align="center">$C_{18}H_{16}ON_2,2HNO_3$,</div>

forms cantharides-green leaflets, m. p. 72° (decomp). The *nitrate* of the ethyl ether, $C_{19}H_{18}ON_2,2HNO_3$, m. p. 84° (decomp), crystallises similarly.

1-p-*Tolueneazo-2-naphthyl methyl ether hydrochloride*,
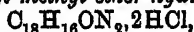
<div align="center">$C_{18}H_{16}ON_2,2HCl$,</div>

crystallises in red needles having a golden lustre. The *hydrobromide*, $C_{18}H_{16}ON_2,2HBr$, forms metallic green needles. The *nitrate*,

<div align="center">$C_{18}H_{16}ON_2,2HNO_3$,</div>

m. p. 77° (decomp.), forms dark red needles with a green metallic lustre. The *nitrate* of the ethyl ether, $C_{19}H_{18}ON_2,2HNO_3$, m. p. 94° (decomp.), crystallises in garnet-red leaflets, which have a golden lustre.

1-o-4-*Xyleneazo-2-naphthol*, $C_{14}H_{16}ON_2$, crystallises in cherry-red needles with a golden lustre, and has m. p. 146°; it dissolves in concentrated sulphuric acid, giving an intense red coloration. The *methyl ether*, $C_{19}H_{18}ON_2$, forms red, prismatic leaflets, m. p. 106°. The *hydrochloride* of the methyl ether, $C_{19}H_{18}ON_2,2HCl$, forms red needles having a golden lustre. The *hydrobromide*, $C_{19}H_{18}ON_2,2HBr$, crystallises in garnet red needles. The *nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, m. p. 87—88° (decomp.), crystallises in coffee-coloured scales, which have a golden lustre. The *ethyl ether*, $C_{20}H_{20}ON_2$, m. p. 94—95°, forms

red needles which have a golden lustre. The *hydrochloride* of the ethyl ether, $C_{20}H_{20}ON_2,2HCl$, crystallises in metallic, coffee-coloured needles. The *hydrobromide*, $C_{20}H_{20}ON_2,2HBr$, forms red needles.

1-m 4-*Xyleneazo-2-naphthyl methyl ether*, $C_{19}H_{18}ON_2$, m. p. 72—73°, crystallises in garnet-red, prismatic leaflets, which have a violet lustre. The *hydrochloride*, $C_{19}H_{18}ON_2,2HCl$, and the *hydrobromide*,
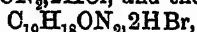
$$C_{19}H_{18}ON_2,2HBr,$$

crystallise in microscopic, red needles. The *nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, forms cantharides-green needles, m. p. 83° (decomp.). 1-m-4-*Xyleneazo-2-naphthylamine*, $C_{18}H_{17}N_3$, crystallises in orange-red leaflets, m. p. 128°; it dissolves in concentrated sulphuric acid, giving a reddish-violet coloration. 1-m-4-*Xyleneazo-2-naphthyl ethyl ether*, $C_{20}H_{20}ON_2$ forms garnet-coloured needles, m. p. 47°. The *hydrochloride*,

$$C_{20}H_{20}ON_2,2HCl,$$

forms coffee-coloured needles, and the *hydrobromide*, $C_{20}H_{20}ON_2,2HBr$, crystallises in garnet-red needles. The *nitrate*, $C_{20}H_{20}ON_2,2HNO_3$, forms cantharides-green needles, m. p. 82°.

1-p-*Xyleneazo-2-naphthyl methyl ether*, $C_{19}H_{18}ON_2$, crystallises in garnet-red, prismatic tablets, m. p. 91—92°. The *hydrochloride*, $C_{19}H_{18}ON_2,2HCl$, forms garnet-red needles, and the *hydrobromide*, $C_{19}H_{18}ON_2,2HBr$, forms coffee-coloured needles. The *nitrate*,
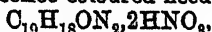
$$C_{19}H_{18}ON_2,2HNO_3,$$

crystallises in cantharides-green laminæ, m. p. 75° (decomp.). The *ethyl ether*, $C_{20}H_{20}ON_2$, crystallises in aggregates of red laminæ, or in needles, m. p. 61—62°. The *hydrochloride*, $C_{20}H_{20}ON_2,2HCl$, forms copper-coloured needles, as does also the *hydrobromide*,
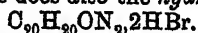
$$C_{20}H_{20}ON_2,2HBr.$$

The *nitrate*, $C_{20}H_{20}ON_2,2HNO_3$, forms dark red, prismatic laminæ, m. p. 71° (decomp.).

The *hydrochloride* of 1-α-naphthaleneazo-2-naphthyl methyl ether, $C_{21}H_{16}ON_2,2HCl$, crystallises in bluish-violet needles, and the hydro-bromide, $C_{21}H_{16}ON_2,2HBr$, forms iridescent, greenish-brown needles.

R. V. S.

Formation of the Azo- and Bisazo-phenols. GIACOMO PONZIO (*Gazzetta*, 1913, **43**, i, 559—562).—Azo- and bisazo-phenols can be prepared very conveniently by keeping benzenediazonium acetate for a short time. If the solution prepared by diazotising 9·3 grams of aniline in the presence of 20 c.c. of hydrochloric acid (D 1·19) is treated with 25 grams of sodium acetate and diluted to a volume of 5 litres, *p*-benzeneazophenol is deposited after keeping for twenty-four hours at the ordinary temperature. The substance forms yellow leaflets, m. p. 154°, although in the literature the m. p. 148° is usually given. Both its acetate and its benzoate exhibit chromoisomerism, for they exist in red and in yellow forms. If phenol is added to the above solution an immediate precipitate of the azo-compound occurs, so that its spontaneous production when the solution is kept is due to inter-action of the diazo-compound with phenol which is slowly formed from it.

If the above-mentioned solution is diluted to a volume of only

500 c.c., 2:4-bisbenzeneazophenol is rapidly deposited by it. In the same way, the corresponding bisazocresol, as well as the azocresol, can be obtained from o-toluidine. R. V. S.

Polyazoxy-compounds. II. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 844—850. Compare this vol., i, 658).—The present paper deals with bisazoxybenzene, previously described (*loc. cit.*). On reduction with aluminium amalgam it yields bisazobenzene (Mills, T., 1895, **67**, 929). By the action of concentrated sulphuric acid at 100°, bisazoxybenzene yields benzeneazobenzeneazophenol (*loc. cit.*), which is identical with that obtained by diazotising aminoazobenzene and treating the product with phenol. This derivative yields an *ethyl ether*, $C_{20}H_{18}ON_4$, which crystallises in red laminæ, melting to a turbid liquid at 138°, becoming then viscous and subsequently limpid again at about 210°. When bisazoxybenzene is treated with concentrated sulphuric acid for some hours at 0°, three substances are formed: (1) a substance, $C_{18}H_{14}O_2N_4$, which forms ruby-red crystals, m. p. 203°; (2) a substance, $C_{18}H_{14}O_2N_4$, which crystallises in shining, orange-yellow laminæ, m. p. 168°; and (3) a substance,

$$C_{18}H_{14}O_2N_4,$$
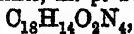
crystallising in deep orange-yellow laminæ, m. p. 148°. The first-mentioned compound (m. p. 203°) is soluble in alkalis and yields a *benzoyl* derivative, $C_{25}H_{18}O_3N_4$ (yellow crystals, m. p. 178°) and an *ethyl* derivative, $C_{20}H_{18}O_2N_4$ (orange-coloured prisms, m. p. 142°, forming a turbid liquid which becomes clear about 180°). The compound of m. p. 168° yields bisazobenzene on reduction, and gives a small quantity of a polybromo-derivative when heated with bromine; it is an isomeride of the bisazoxybenzene of m. p. 155°

$$[Ph \cdot N{:}NO \cdot C_6H_4 \cdot NO{:}NPh,$$
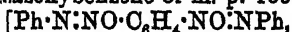
termed the β-form], and is assigned the formula

$$Ph \cdot NO{:}N \cdot C_6H_4 \cdot N{:}NOPh$$

(α-form). The compound of m. p. 148° is probably a third isomeride (γ-form), to which the constitution $Ph \cdot NO{:}N \cdot C_6H_4 \cdot NO{:}NPh$ is ascribed. R. V. S.

Colloidal Chemical Studies on the Proteins. HUGO ROHONYI (*Biochem. Zeitsch.*, 1913, **53**, 179—209).—Solutions of proteoclastic ferments possess the property of precipitating proteins and albumoses from their solutions under certain conditions. The latter are as follows: (1) The solutions should contain at the most only traces of neutral salts, as the precipitates are soluble in salt solutions; (2) as the precipitates are soluble in acids and alkalis, precipitation only takes place within narrow limits of the hydrogen-ion concentration; (3) the reacting substances must be present in certain definite proportions, as the precipitates are often soluble in excess of either reagent. The reactions can take place even after activation of the ferment, and the precipitates are probably complexes of the protein and ferment. If acid is added to protein solutions, and the conductivity curve is plotted, the formation of precipitates causes no discontinuity in the curve. The combination of acids with proteins depends there-

fore on the absolute amount of protein present, and is independent of the surface of the latter. Paranuclein is not a product of hydrolysis, but a caseinogen-caseose complex. The paranuclein of Brailsford Robertson is a complex compound of caseose and a protein contained in Grübler's pepsin preparation. It is not formed when certain other preparations of pepsin are employed. Reasons are given for supposing that the so-called plasteins are complex albumose enzyme compounds.

S. B. S.

The Precipitation of Egg-Albumin by Ammonium Sulphate. The Theory of the "Salting Out" of Proteins. HARRIETTE CHICK and CHARLES J. MARTIN (*Biochem. J.*, 1913, 7, 380—398).— The precipitation of egg-albumin by ammonium sulphate is, as Spiro showed for sodium sulphate and caseinogen and gelatin, due to the separation of the system into a protein-rich phase and a watery phase, and is to a certain extent analogous to the salting out of alcohol. The first effect of concentrated salt is to withdraw water from the protein aggregates; a surface tension is in consequence developed at the interfaces, which causes the protein particles to aggregate, thus dividing the system into two distinct phases (precipitate and filtrate). The various factors which influence the precipitation are discussed at length; a dominating influence is the concentration of hydrogen ions.   W. D. H.

The Molecular Weight of Hæmin. HANS FISCHER and AMANDUS HAHN (*Ber.*, 1913, 46, 2308—2309).—Ebullioscopic measurements in pyridine solution indicate for hæmin a molecular weight of 651, and therefore a molecular formula $C_{34}H_{32}O_4N_4FeCl$; the trustworthiness of the method is confirmed by numbers indicating the molecular weight 655 for the complex iron salt of mesoporphyrin,

$$C_{34}H_{36}O_4N_4FeCl.$$

The solution of free haematoporphyrin in pyridine appears to be colloidal, for the elevation in the b. p. of the solvent is so slight as to indicate a molecular weight over 3000 (compare Piloty and Dormann, A., 1912, i, 519).   D. F. T.

Hæmatin. III. Chemistry of the Formation of Hæmatoporphyrin. WILLIAM KÜSTER and PAUL DEITLE (*Zeitsch. physiol. Chem.*, 1913, 86, 51—76. Compare A., 1912, i, 670).—The age of hæmin preparations makes a considerable difference in their behaviour towards hydrogen bromide. Whereas freshly prepared hæmin yields almost exclusively hæmatoporphyrin and ferric iron, old hæmin preparations give both ferrous and ferric iron and much by-product. The changes in hæmin on keeping obviously take place at the centres which play a part in the formation of hæmatoporphyrin; these are considered to be the vinyl groups.

Hæmatoporphyrin is very readily esterified with methyl alcohol and hydrogen chloride. The product is a dimethyl derivative, insoluble in sodium carbonate, m. p. 142°, proving that the two carboxyl groups were present in hæmin, whereas the hydroxyl groups were formed

during the formation of hæmatoporphyrin. The ester is readily hydrolysed by sodium hydroxide.

A tetramethyl hæmatoporphyrin is obtained on prolonged heating with methyl alcohol and hydrogen chloride; the non-crystalline product has m. p. 81°.

A tetramethyl derivative is also obtained when the intermediate product formed by the action of hydrogen bromide in acetic acid on hæmin is warmed with anhydrous methyl alcohol. This substance, *methyl dimethoxydihydrohaematerindicarboxylate*, forms large crystals, m. p. 128°.

On hydrolysis the tetramethyl derivative forms *haematoporphyrin dimethyl ether*, a bright scarlet, amorphous powder, m. p. 105°, soluble in alkali; the *hydrochloride* is crystalline, forming needles; the *zinc* salt is bright red, and blackens at 100°. When esterified, it yields the original tetramethyl compound again.

A further argument against the assumption that hæmin contains, as supposed by Piloty, lactam junctions is afforded by the discovery of a dimethoxydihydrohæmin amongst the products of the action of methyl alcohol on the above intermediate product.

Hæmatoporphyrin forms a silver salt containing two atoms of metal; its dimethyl ether forms one with three atoms of metal; both compounds fix three molecules of ammonia. Hæmatoporphyrin forms a stable dihydrochloride, whereas the hydrochloride of the dimethyl ether is very unstable, and that of the dimethyl ester could not be prepared. This behaviour indicates betaine formation between the nitrogen and the methyl group of the ester, and to a less extent the methyl group of the dimethyl ether. Prolonged action of concentrated hydrochloric acid displaces one of the methyl groups, forming a mono-methyl ether, which, however, has a stable monohydrochloride.

The *dimethyl* ester of *anhydrohaematoporphyrin* forms an intense scarlet, bulky powder, m. p. 140—141°.   E F. A.

Hæmatin. V. Methylation of Hæmin and the Addition of Bromine to Chlorodimethylhæmin and Bromodimethyl-hæmin. WILLIAM KÜSTER and ALFRED GREINER (*Zeitsch. physiol. Chem*, 1913, 86, 185—205).—Dimethylhæmin is the dimethyl ester of the dibasic acid hæmin. Reasons are discussed for attributing a different degree of acidity to the two carboxyl groups, particularly the behaviour of hæmin to methyl sulphate In strongly alkaline solution there is no action, in weak alkali a monomethyl derivative is formed, whereas in acid solution dimethylhæmin is formed without difficulty, it is identical with the product produced by means of methyl alcohol and hydrogen chloride. The monomethyl derivatives from hæmatin and dehydrochlorohæmin did not crystallise.

When bromine in chloroform solution acts on dimethylhæmin, bromine is absorbed without the liberation of hydrogen bromide; more or less of the chlorine of the hæmin is replaced by bromine, so that a complex mixture results. In acetic acid solution, however, a chlorodimethylhæmin dibromide is obtained. Very little of a tetra-bromo-product is formed. In a similar manner, bromodimethylhæmin dibromide is formed. It can be crystallised from acetic acid.

No methyl is eliminated by the action of aniline on dimethylhæmin. The dimethyl dehydrochlorohæmin so obtained is partly soluble in ether; the two portions differ in the amount of chlorine they contain. When converted into the corresponding bromodimethylhæmins, compounds which differ in their crystalline habit are obtained. Aniline reconverts both of these into dehydrobromo-products which are soluble and insoluble in ether respectively.

Bromine may be eliminated from hæmin dibromide by means of aqueous alkali, sodium methoxide, or by zinc and acetic acid. On oxidation one molecule of the dibromide yields two molecules of hæmatic acid. The conclusion is drawn that the addition of bromine takes place at the vinyl residues.

The complex $C_{32}H_{34}N_4$ is termed *hæmaterin*, and its dicarboxylic acid, $C_{34}H_{34}O_4N_4$, *hæmaterindicarboxylic acid*. Hæmin, bromohæmin, and hæmatin are thus complex chloro-, bromo- and hydroxy-ferric salts, of this acid.   E. F. A.

Tetrachloromesoporphyrin.   HANS FISCHER and HEINRICH RÖSE (*Ber.*, 1913, 46, 2460—2466).—On the cautious addition of fuming hydrochloric acid and hydrogen peroxide to mesoporphyrin dissolved in glacial acetic acid, the hydrochloride of a dye crystallising in green needles is obtained. This is *tetrachloromesoporphyrin*, chlorine being substituted for hydrogen in the four methine groups uniting the pyrrole nuclei in pairs. On reduction of the tetrachloro-compound with sodium amalgam, porphyrinogen is obtained, whereas mesoporphyrin results on heating with sodium methoxide at 220—230°. The green compound is also formed when chlorine is passed into a solution of mesoporphyrin in acetic acid. Reduction with acetic acid and hydrogen iodide converts it into mesoporphyrin again and not into porphyrinogen. One of the chlorine atoms is much less firmly held than the others.
                                                        E. F. A.

Chondroitin-sulphuric Acid.   PHŒBUS A. LEVENE and FREDERICK B. LA FORGE (*J. Biol. Chem.*, 1913, 15, 69—79).—Chondrosine, the nucleus of chondroitin-sulphuric acid, when hydrolysed by means of sodium amalgam yields glycuronic acid, identified by the phenyl- and *p*-bromophenyl-hydrazine derivatives.

The glycuronic acid is not bound to the amino-group of the second component, since the nitrous acid process demonstrates the presence of an unsubstituted amino-group in chondrosine. Neither does the carbonyl group of glycuronic acid take part in the linking. On oxidation of chondrosine with nitric acid a product is obtained which on distillation with hydrochloric acid gives rise to a minimal quantity of furfuraldehyde, whilst chondrosine yields the quantity required by a complex composed of one molecule of glycuronic acid and one of a carbohydrate of about the same molecular weight. The oxidation product does not contain free saccharic acid until it has been hydrolysed with alkali. Hence chondrosine contains saccharic acid

in a conjugated form. In chondroitin-sulphuric acid both the carboxyl and the amino-groups are combined with other radicles.

<div align="right">E. F. A.</div>

Identity of Rennet, Casease, and Trypsin from the Same Latex. Existence of Two Types of Vegetable Proteolytic Ferments. C. GERBER (*Compt. rend.*, 1913, **157**, 241—243. Compare A., 1907, i, 1100; 1908, i, 745; 1909, i, 74, 278; ii, 512, 824; 1910, ii, 64; 1911, ii, 647; 1912, ii, 801; this vol., i, 806).—Rennet, casease, and trypsin obtained from the same latex exhibit the same resistance to heat, and their diastatic actions are influenced in the same manner by certain electrolytes and by certain substances, such as lactalbumin and lactoglobulin, which accompany the substances on which they act. A study of these enzymes obtained from *Ficus carica* and *Broussonetia papyrifera* shows further that their diastatic actions obey the same laws of mass, time, and temperature, and their variations in intensity, seasonal for the same plant or individual for the same period, are strictly parallel. From these results the author maintains that rennet, casease, and trypsin from the same latex are but three different or successive aspects of the same diastase, coagulating the milk and carrying the hydrolysis of the casein and the fibrin to the formation of amino-acids. The characteristics distinguishing the three proteolytic actions of the latex are due to differences in the action of calcifying and decalcifying salts, acids, and bases on the coagulation and diastatic digestion of milk. The proteolytic ferments of the latex belong to two groups, the one having for type the proteolytic disastase of *Ficus carica* and the other that of *Broussonetia papyrifera*, the former being inactive towards milk, whilst the latter are active.

<div align="right">W. G.</div>

Action of Hydrogen Chloride on a Diastase Preparation which had been Altered by Heating. IX. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **86**, 322—339).—A diastase preparation of which the activity had been destroyed by heating was rendered slightly active again by treatment with dry hydrogen chloride and subsequently removing this in a vacuum. It is considered that the original active groups in the enzyme have not been restored by the acid, but that this has attacked other atomic groupings, which become active as enzymes when the hydrogen chloride is removed.

<div align="right">E. F. A.</div>

Identity of the Hydrolytic and the Synthetic Activities of Emulsin. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.* 1913, [vii], **8**, 15—19).—Emulsin hydrolyses the β-glucosides of the alcohols and causes the combination of dextrose with the alcohol to a β-glucoside. Both these reactions are incomplete, and there is a tendency to attain an equilibrium. The position of this equilibrium is independent of the quantity of emulsin added and of the temperature, but it varies with the strength of the alcohol and with the amount of

dextrose present. It is shown experimentally that in a solution containing 30·2% by weight of methyl alcohol, and equivalent quantities of dextrose or β-glucoside together with emulsin, the rates of hydrolysis and synthesis are the same, and the same point of equilibrium is reached from both directions. The probability of emulsin acting synthetically in plants is emphasised.   E. F. A.

Reversibility of Enzyme Action: a-Glucosidase and a-Methylglucoside. ÉMILE BOURQUELOT and ÉMILE VERDON (*J. Pharm. Chim.*, 1913, [vii], 8, 19—21).—Bottom yeast extract was allowed to act in solutions containing 20 grams per 100 c.c. of methyl alcohol and equivalent quantities of dextrose or a-methylglucoside. In about twenty-nine days both solutions had the same rotatory power, indicating that the same equilibrium is attained starting from either end.   E. F. A.

The Rennin Coagulation of Milk from a Colloid Chemical Standpoint. JEROME ALEXANDER (*Eighth Inter. Cong. App. Chem.*, 1912, 6, 12—14).—Silver nitrate gives a clear silver chloride sol in presence of fresh lactalbumin, but, after digestion with pepsin, lactalbumin does not exert the influence of a protective colloid. The action of acids or rennin on milk is thus to destroy the colloidal protection of the lactalbumin for the unstable, irreversible suspensoid, casein (compare A., 1910, i, 530).   J. C. W.

New Function of the Catalyst termed "Peroxydase" and the Biochemical Transformation of Orcinol into Orcein. JULES WOLFF (*Eighth Inter. Cong. App. Chem.*, 1912, 26, 417—419. Compare A., 1912, i, 928).—Experiments are described which show that dilute solutions of orcinol are slowly oxidised by ammonia with production of orcein. This action is greatly accelerated by peroxydase, the effect of which is to promote the formation of the colouring matter rather than to increase the amount of oxygen absorbed.   E. G.

The Catalase of the Liver. LEONOR MICHAELIS and H. PECHSTEIN (*Biochem. Zeitsch*, 1913, 53, 320—355).—The ferment solution employed was a highly diluted extract of calves' liver, and hydrogen peroxide was used as the substrate. The course of the action was followed by determining the rate of destruction of the peroxide by titration with permanganate solution. It was found that for the catalase reaction, the ordinary equation $\Phi.t = f(x)$, where Φ is the quantity of the ferment, $t =$ time of action, and $f(x)$ a characteristic function of the ferment, does not hold, but must be replaced by the equation $\Phi^n.t = fx$, in which n is of the approximate value of 1·35, but varies slightly during the course of the reaction. The deviation from the ordinary law is due to the fact that the ferment is acted on by the hydrogen peroxide, as its action is weakened by previous treatment with this reagent. Oxygen itself does not act, and the same results are obtained when the reaction is carried out in a current of hydrogen

or in a corked flask. As determined by the wandering of the ferment in an electrical field, where the [H]˙ concentration was varied by different acetate mixtures, the isoelectric point of the ferment was found to be $4\cdot31.10^{-6}$. The rate of ferment action was determined in low salt concentrations (acetate mixtures) with varying hydrogen-ion concentrations. By the graphical methods already employed by Michaelis and his pupils, the amounts of ferment active in solutions of different hydrogen-ion concentrations were determined. The optimal condition of action is attained just after the hydrogen-ion concentration becomes less than the isoelectric point of the ferment. The conclusions drawn are, that catalase is an ampholyte with the acid dissociation constant $2\cdot88 \times 10^{-5}$, and that the catalytic action on hydrogen peroxide is due to the anions and electrically neutral particles. Neutral salts inhibit the action (hence all the experiments on the effect of the [H]˙ concentration were carried out with very dilute acetate mixtures). The inhibitory action is more marked in the neighbourhood of the isoelectric point than in more acid solutions. The conclusion is drawn that the anions of the salt exert the chief action, and affect chiefly the electrically neutral particles of the ferment. The order of the inhibitory action is $SO_4 > Cl > \text{acetate} > NO_3$. S. B. S.

Constitution of the Mercuriated Products of Acetylene. WILHELM MANCHOT and JULIUS HAAS (*Annalen*, 1913, **399**, 123—154). —Phenylacetylene and an excess of aqueous mercuric chloride at 47—50° yield a *substance*, $C_{16}H_{11}O_2Cl_5Hg_5$ or $C_{16}H_{13}O_3Cl_5Hg_5$, in which the mercury is very firmly held. It does not react with aqueous sodium hydroxide or ammonia, but yields mercuric sulphide by treatment with ammonium sulphide. By treatment with dilute hydrochloric acid, it yields phenylacetylene and acetophenone. This decomposition indicates that the substance is an additive compound of an acetylene, not a mercuriated ketone, and consequently the constitution may be $Hg(C:CPh)_2,2HgCl_2,HgO,HgCl\cdot OH$, which is supported by the fact that the same substance is produced by the action of an excess of aqueous mercuric chloride on mercury phenylacetylide in the presence of a little hydrochloric acid at 50°.

A similar *substance*, $C_{16}H_{10}OBr_4Hg_4$, is produced by the interaction of phenylacetylene and aqueous mercuric bromide at 50°. It also does not react with sodium hydroxide or ammonia, yields mercuric sulphide by treatment with ammonium sulphide, and is decomposed by hydrochloric acid to form acetophenone and phenylacetylene. Probably, therefore, its constitution is $Hg(C:CPh)_2,2HgBr_2,HgO$. Both of these substances, suspended in chloroform in a freezing mixture, absorb a large amount of bromine; ultimately, however, hydrogen bromide is evolved.

Piperonylacetylene reacts with mercuric chloride and bromide to form substances which are analogous to the preceding, but which yield only acetopiperone by treatment with hydrochloric acid. This is due to the fact that the piperonylacetylene which is initially formed unites with water with extraordinary ease in the presence of hydrochloric acid. Since the preceding substances are additive compounds of acetylenes,

it is probable that the substance obtained by the action of acetylene itself on aqueous mercuric chloride is an additive compound, not a mercuriated aldehyde, $C(HgCl)_3$·CHO, as suggested by Biltz and Mumm. The latter view is almost certainly incorrect, because the substance exhibits the reactions of mercurous and of mercuric salts. The substance, which is also obtained from mercury acetylide and aqueous mercuric chloride, yields only acetaldehyde by treatment with dilute hydrochloric acid, but is decomposed by ammonium sulphide to form acetylene and acetaldehyde. Probably, therefore, its constitution is $C_2Hg,HgCl_2,HgCl,H_2O$. A substance, exhibiting properties similar to those of the preceding substance is obtained from acetylene or mercury acetylide and an excess of aqueous mercuric bromide.

It is evident from the behaviour of the preceding mercury compounds that mercury can be retained very firmly in an organic compound without necessarily being attached to carbon in the place of hydrogen atoms.   C. S.

Physiological Chemistry

A Calorimeter for Small Animals. FRANZ TANGL (*Biochem. Zeitsch.*, 1913, **53**, 21—35).—The calorimeter is constructed on the compensation principle. Two exactly similar cylinders of copper, each insulated in a Dewar flask, are connected with one another by constantan wires, so as to form thermoelectric couples, and a Broca galvanometer is placed in circuit between the two, so as to indicate any differences of temperature between them. The whole apparatus is immersed in a large thermostat. The animal is placed in one cylinder in a cage, and the other cylinder contains a similar cage without an animal. The heat produced by the animal in one cylinder is approximately compensated for by the passage of a known electric current through the other, which produces an experimentally measurable quantity of heat. The small differences of heat in the two cylinders can be measured by the deflexions produced when the galvanometer is thrown into the circuit. The galvanometer deflexions can be calibrated by passing two measured but slightly different currents through the two cylinders. The total heat produced by the animal is therefore calculated both from the compensation current and the galvanometer readings; the calorimeter can also serve as a respiration calorimeter, by the analysis and measurement of the air led in (which is first carefully warmed to the temperature of the thermostat by a long passage through pipes immersed in the water it contains), and the analysis of the expired air, in the usual manner adapted for such calorimeters. Illustrations in the text indicate the exact method of construction of the apparatus (compare A. V. and Miss Hill, this vol., i, 666).   S. B. S.

The Response of the Respiratory Centre to Carbon Dioxide, Oxygen, and Hydrogen Ion Concentration. J. M. H. CAMPBELL, CLAUDE E. DOUGLAS, JOHN S. HALDANE, and F. G. HOBSON (*J. Physiol.*, 1913, **46**, 301—318).—A rise of 0·2% or 1·6 mm. in the pressure of carbon dioxide in the alveolar air doubles the pulmonary ventilation. A corresponding diminution causes apnœa. The alveolar oxygen pressure can be varied within wide limits without affecting the excitability of the respiratory centre to carbon dioxide. Summation of inhibitory vagus stimuli plays no part in causing apnœa in man. What the respiratory centre really responds to is the balance of hydrogen ion concentration in the blood. This balance is exquisitely regulated, probably for the most part by the kidneys. W. D. H.

Respiratory Mechanism in the Duck. J. B. ORR and ALEXANDER WATSON (*J. Physiol.*, 1913, **46**, 337—348).—In the duck, carbon dioxide in the inspired air acts inhibitingly on respiration. Lack of oxygen is stimulating to the respiratory rhythm. The vagus nerves probably play an essential part in the maintenance of respiratory movements. W. D. H.

The Influence of the Cerebrum on the Metabolism of Energy and of Matter. KARL HANNEMANN (*Biochem. Zeitsch.*, 1913, **53**, 80—99).—The experiments were carried out on frogs, the respiratory exchanges of which were measured in chambers made according to a method described in the text, from ordinary laboratory desiccators. These exchanges were measured in the cases of intact animals, and animals from which different parts of the brain had been extirpated. It was found that the extirpation of either the whole brain, or only the large hemispheres, or the optic lobe led to a considerable increase in the gaseous exchange, lasting for several days. Both the oxygen consumption and the carbon dioxide output were increased, especially the latter, which was not so much increased, however, when only the hemispheres were removed. The increase in the gaseous exchanges is accompanied by an increased heat production, which was measured in a Tangl calorimeter. S. B. S.

The Influence of Narcosis on the Gaseous Metabolism of the Brain. FRANZ G. ALEXANDER and STEPHAN CSERNA (*Biochem. Zeitsch.*, 1913, **53**, 100—115).—Dogs were used for the purpose of the experiments. They were tracheotomised under ether narcosis, hiradin was injected into the jugular vein and the femoral artery, and the sinus longitudinales was laid bare for the purpose of collecting blood samples. By means of blood-gas analyses, the gaseous metabolism could be determined when the animal had recovered from narcosis, and when it was under the influence of various anæsthetics. The rate of blood-flow was measured by Barcroft's method. It was found that the specific gaseous exchanges of the blood were considerable, the oxygen consumption of this organ being about 0·36 c.c. per gram per minute. During

narcosis the gaseous metabolism sinks considerably—from 60 to 90%
according to depth of the narcosis.   With ether, the carbon dioxide
output diminishes less than the oxygen consumption; the reverse
is the case in morphine narcosis.   The action of various narcotics
is different, and this fact must be taken into account in all theories
dealing with the phenomenon.   In narcosis with magnesium
sulphate, the higher centres of the nervous system are the last to
be paralysed.   The actual narcosis is preceded by a stage of
excitation, during which the gaseous metabolism of the brain is
increased.   S. B. S.

Blood-lipoids and Phagocytosis.   B. STUBER (*Biochem. Zeitsch.*,
1913, **53**, 493—500).—The addition of cholesteryl esters of oleic
and palmitic acids inhibits phagocytosis *in vitro*, and with the latter
substance also *in vivo*, when the blood is withdrawn (from cats)
half an hour after the injection.   Owing to the rapidity with which
clot formation takes place, experiments could not be extended
beyond this period, and for the same reason no *in vivo* experiments
were possible with the oleic acid derivative, which very readily
renders the blood so clottable that it clots directly on opening the
veins.   The inhibition is not removed by mixing the cholesterol
derivatives with lecithin, as is the case with free cholesterol.
Cholesteryl benzoate and acetate are without action on phagocytosis,
in which substances the free hydroxyl group no longer exists, and
to this group is ascribed the inhibitory action of cholesterol and its
derivatives on phagocytosis.   Wright's theory of opsonins is discussed,
and it is suggested that the opsonic index is not due to specific
opsonins, but rather to the different states of the lipoids in the
blood.   S. B. S.

The Effect of Fatty Acids and Soaps on Phagocytosis
HARTOG J. HAMBURGER and J. DE HAAN (*Proc. K. Akad. Wetensch.
Amsterdam*, 1913, **15**, 1290—1297).—Propionic acid itself diminishes
phagocytic action (as determined by Hamburger's charcoal method),
whereas sodium propionate increases it, within wide limits of con-
centration of the salt.   The former action is to be ascribed to the
hydrogen ions, whereas the latter action is due to the action of
the salt on the surface tension of the water.   This constant is
diminished, and this facilitates the pseudopodial action of the
phagocytes.   This action of sodium propionate and soaps is to be
distinguished from the action of fat-dissolving substances, which
exert their action owing to the fact that they dissolve in lipoids.
                                                             S. B. S.

The Blood of Ascidians.   III.   MARTIN HENZE (*Zeitsch. physiol.
Chem.*, 1913, **86**, 340—344).—The author's previous work has shown
that organic vanadium compounds occur in the blood-corpuscles of
Phallusia, and that these cells have an acid reaction due to sulphuric
acid.   It is now shown that vanadium also occurs in the blood
of other ascidians (*A. mentula, A. fumigata, Ciona intestinalis*,
and *Diazonia violacea*); in *Cynthia papillosa* its presence is
uncertain.

Much of the present paper deals with the kinds of blood-corpuscle found, and their reactions with staining fluids. The nature of the pigment in the red cells of *Ascidia mentula* is uncertain; it is not a lipoid, and is insoluble in all common reagents.

W. D. H.

The Application of the Second Law of Thermodynamics to Processes in the Animal Organism. JULIUS BÁRON and MICHAEL PÓLÁNYI (*Biochem. Zeitsch.*, 1913, **53**, 1—20).—A knowledge of the changes of free energy in the animal organism can be arrived at by the application of Nernst's heat theorem. These changes of free energy were calculated for the individual products taking part in metabolism. It was found that the changes correspond very nearly with the heat production. The results indicate that the processes in the organism take place in accordance with the second law of thermodynamics only when the organism does not work with absorption of heat. The thermodynamical efficiency of mechanical work and of fat synthesis from sugar was calculated, and the trustworthiness of the theory from the point of view of the second law was confirmed.

S. B. S.

The Influence of the Character of the Nutrition on the Metabolism During a Succeeding Period of Starvation. ARTHUR SCHLOSSMANN and HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1913, **53**, 265—299).—Dogs were starved for some days, and then fed with different diets, in one case containing large amounts of fats, in another large amounts of carbohydrates, and in a third case, chiefly proteins. When the animals had attained their original weights again on these diets, a short period of starvation was interposed, during which the metabolism was investigated by the ordinary methods. As a result of these and earlier experiments, the conclusion was drawn that the metabolism during a period of starvation in both man and dogs depends to a large extent on the character of the nutrition ingested in the foregoing period, and this influence can be demonstrated even when the effects of the last meal taken have vanished. The organism has got accustomed to the utilisation of either fats, carbohydrates, and proteins, and the habit thus acquired still lasts even when the animal is deprived of food. This influence is demonstrated chiefly by the respiratory quotients, which remain similar during starvation to those obtained during the period of feeding. The influence of the fat diet lasts longer than that of the carbohydrate diet, as the reserve glycogen is soon used up. Thus, in the case of the dog fed on fats, on the fifth as well as on the second day of starvation about 90% of the calories are derived from the fat, and 3% from carbohydrates. In the case of the carbohydrate-fed dog, on the second day of starvation 21% of the calories are derived from carbohydrates, and 65% from fats; and on the fifth day, only 8% from carbohydrates and 79% from fats. The organism can therefore be "trained" to adapt itself to various diets.

S. B. S.

The Action of Carbohydrates on the Energy Metabolism.
PAUL HÁRI (*Biochem. Zeitsch.*, 1913, 53, 116—139).—The experiments
were carried out with the employment of the Tangl respiration
calorimeter, and both the heat production and the nitrogen and
carbon metabolism were investigated at the same time. When
dextrose was subcutaneously administered to mice in 10% solution,
in quantities corresponding with 10 grams per kilo. of body-weight,
it caused a rise in the heat production of 8—13·2%. In quantities
of 28—32 grams per kilo. of body-weight, when administered to
starving rats, it caused a rise of 28—29·9%. This rise can be
partly explained as a result of sugar intoxication. The heat thus
produced is chiefly lost by radiation when the sugar is administered
in concentrated solutions, but chiefly by water evaporation when
given in dilute solution.   S. B. S.

The Biochemical Synthesis of the Fatty Acids. (Miss) IDA
SMEDLEY and (Miss) EVA LUBRZYNSKA (*Biochem. J.*, 1913, 7, 364—374).
—The hypothesis that pyruvic acid formed in the body from
carbohydrates is the starting point for the synthesis of the fatty
acids, is supported by a number of pieces of evidence, and
equations are given to represent the series of reactions which occur
                                                            W. D. H.

Fatty Acid Esters of Dextrose. W. R. BLOOR (*Eighth Inter.
Cong. App. Chem.*, 1912, 19, 29—36).—Attention is called to the fact
that fats are not completely metabolised in the absence of carbo-
hydrates, as is witnessed by the fact that such products as
β-hydroxybutyric acid, acetoacetic acid, etc., are excreted during
starvation. The suggestion is made that sugars may act cata-
lytically in the destruction of the fats in the animal body. It
was therefore of interest to prepare dextrose esters of fatty acids
and to investigate their action when administered to animals.
These esters were prepared by the interaction of the acid chloride
on dextrose in pyridine solution, and a preliminary account of
several such esters is given. They readily form colloidal solutions
with water. For physiological experiment a mixture of the esters
prepared from the fatty acids of cocoa-nut oil was employed.
When administered to cats by the mouth, these esters are readily
absorbed (up to more than 80%). They do not appear to be
adapted to administration either intraperitoneally or intravenously.
In the former case, they act as an irritant foreign substance, and
in the latter case they can act injuriously, even producing death
of the animal   S. B. S.

Is Inulin a Glycogen Former? ALFRED OPPENHEIM (*Chem.
Zentr.*, 1913, ii, 371; from *Zentr. Physiol.*, 1913, 27, 264—267).—
Rabbits freed from glycogen by injections of strychnine were fed
with inulin. Some glycogen was formed in the liver, and a good
deal in the muscles. Since feeding with lævulose leads to the
formation of glycogen in the liver, it is assumed that most of the
inulin administered passes the liver and is converted into glycogen
in the muscles.
                                                            E. F. A.

Action of the Digestive Juices on Alicyclic Compounds. JUHO HAMALAINEN (*Chem. Zentr.*, 1913, i, 2052; from *Skand. Arch. Physiol.*, 1913, **29**, 60—67).—When alicyclic compounds are shaken for ten hours at 37° with gastric juice, they become partly hydrated—the hydrocarbons the most easily, and the ketones the least so. Menthene, limonene, terpinolene, pinene, nopinene, and dihydrocarveol give rise to menthanol, terpin, terpineol, etc. Only terpinene and fenchene proved resistant. E. F. A.

Influence of the Melting Point of Non-emulsified Fats on their Rate of Disappearance from the Stomach. A. VON FEJÉR (*Biochem. Zeitsch.*, 1913, **53**, 168—178).—Various fats were mixed with a standard diet and administered to dogs. After a given interval these test-meals were quantitatively removed from the stomachs by a form of stomach-tube, which is described and illustrated in the text, and the fat content of the vomit was then analysed. It was found that the higher the melting point and viscosity of the fat, the more slowly it disappeared from the stomach. The fats, after emulsification with food, disappear more rapidly than when administered in a non-emulsified form. When not administered with foods, these disappear even more slowly still, with the exception of the liquid olive oil. Fats also inhibit the disappearance of the other food constituents from the stomach, and the more viscous fats exert the greater inhibitory action in this respect. A fat added to foods readily separates from other food constituents in the stomach, and is afterwards digested independently of them in the intestine. S. B. S.

The Influence on Nitrogenous Metabolism of Feeding on Sodium Nitrate. ERICH GRAFE and H. WINTZ (*Zeitsch physiol. Chem*, 1913, **86**, 283—314).—Experiments on dogs and pigs are recorded with sodium nitrate similar to those previously published in relation to ammonium salts. In one of the four experiments there was no retention of nitrogen; in the other three, from 10—15% of the nitrogen was retained. Large doses exert a toxic action and increase the output of nitrogen. Hypotheses are advanced to explain the retention of nitrogen W. D. H.

Utilisation of Individual Proteins by Man as Influenced by Repeated Fasting. PAUL E. HOWE and PHILIP B. HAWK (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 145—147).—The method of experiment was to administer to the same individual after a two days' fast, a standard diet containing 12·12 grams of nitrogen and 2500 cal. of energy. This diet was continued for two days, and was then increased for another two days, so that 18·18 grams of nitrogen and 3750 cal. were taken. Two days' fast then succeeded, and was followed by another five days of feeding with the quantities given above, but with nitrogen from another protein. By alternation of two fast days and five feeding days, in which various proteins were employed, the dietetic values of the latter

could be ascertained. The most efficiently utilised proteins were found to be meat and gliadin, of which 97·5% was absorbed, followed by plasmon, milk, and "standard" diet. The substances most efficient in maintaining a nitrogenous equilibrium (in both cases under the conditions of experiment, positive) were, however, meat and milk. It is noteworthy that in both cases the proteins were of animal origin.   S. B. S.

Nuclein Metabolism. MAX DOHRN (*Zeitsch. physiol. Chem.*, 1913, **86**, 130—136).—The results of an experiment in which 10 grams of nucleic acid were consumed in addition to a diet consisting of bread, 300 grams; butter, 80 grams; apples, 250 grams; eggs, 200 grams, and milk, 2 litres, showed that the nitrogen in the form of carbamide is not increased during the nucleic acid period. The nitrogen in uric acid increased 50%, or 9·7% of the nitrogen in purine bases. The rest of the nitrogen as purine bases was not recovered. The phosphoric acid increased considerably, the amount found in the urine and fæces exceeding the amount supplied by 0·76 gram. The results indicate that almost all the nucleic acid underwent cleavage before resorption, and that the slight increase in uric acid is due to resorbed bases.   N. H. J. M.

The Action of the Iron in Blood-powder on the Iron Metabolism when this Product is Administered to Animals. JULIUS GRÓH (*Biochem. Zeitsch.*, 1913, **53**, 256—258).—By the addition of blood-powder to a standard diet administered to pigs, no alteration was caused in the iron balance in the animal, the additional iron from the blood ingested being excreted in the fæces.   S. B. S.

The Localisation and Detection of Peroxydases in the Digestive Tract. ARTHUR SCHEUNERT, WALTER GRIMMER, and PETER ANDRYEWSKY (*Biochem. Zeitsch.*, 1913, **53**, 300—319).—A trustworthy oxydase reagent is guaiacol tincture, to 100 c.c. of which have been added 0·1 -0·2 c.c. of 3% hydrogen peroxide solution. This reagent is capable of detecting an oxydase in milk, saliva, etc., which contain a peroxydase, but not with blood, unless a superoxide solution, such as turpentine oil, ethyl hydroperoxide, etc., is also added. Rothenfusser's reagent (*p*-phenylenediamine + guaiacol) and the potassium iodide starch reagents are not trustworthy for the detection of oxydases. The extracts of tonsils contain no oxydase, the sublingual glands contain large quantities of the ferment, whereas the submaxillary and parotid glands vary largely as to oxydase content in different animals; the same is true with reference to the mucous membrane of the stomach and the small intestine. Liver extracts are free from substances giving the blue reaction with guaiacum tincture. Furthermore, the ferment giving this reaction is not identical with the ferment causing the oxidation of formic acid, as several tissues give one reaction, but not the other. The guaiacol peroxydase of the submaxillary gland of the ox possesses a considerable but not complete resistance to digestion with trypsin.   S. B. S.

Fluorine in the Animal Organism. III. Brain, Glands, Muscles, Blood, Milk, Excretions. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1913, **157**, 94—100. Compare this vol., i, 677, 789).—Like phosphorus, fluorine exists in all animal organs and tissues, but in very varying proportions, the dental enamel having the highest content, 180—118 mg. per 100 grams of dry matter, and the muscle the lowest with 0·6—0·15 mg. per 100 grams. There is a fairly constant relation between the phosphorus and fluorine contents of the various organs, except in the case of the incompletely formed organs of young animals, the excretions, the dental enamel, and the blood. The fluorine increases with the phosphorus without being directly proportional to it. In the same organ the quantity of fluorine varies greatly with age. It increases generally up to the adult age, and then diminishes as the organ begins to degenerate. Muscular tissue is remarkably poor in fluorine. The fluorine content of human milk is very low, but, as in the case of phosphorus, it is about four times as great in cow's milk. About 1 mg. of fluorine per day is excreted by man, and since the amount of fluorine supplied by the food greatly exceeds this, the difference must be due to epithelial desquamation, loss of hair, growth of nails, etc W. G.

The Lipocytic Constant. Content of the Tissues in Phosphorus-containing Lipoids. ANDRÉ MAYER and GEORGES SCHAEFFER (*Compt. rend.*, 1913, **157**, 156—159. Compare this vol , i, 424). —In different individuals of the same species the content of phosphorus in the lipoid form in a given organ is practically constant, but it varies from tissue to tissue in the same animal. For different animal species the values found for a given organ are very close. This phosphorus content of the different organs does not seem to vary during inanition, but rather appears to be the measure of a fundamental and permanent constituent of the cells. In certain cellular types the ratio, fatty acids/phosphorus in lipoid form, is remarkably constant, but in certain organs, for example, the muscles, the ratio has a value pointing to the presence of reserves of neutral fats in these organs. The content of a fresh tissue in phosphorus, in lipoid form, is characteristic of the tissue. In all the species examined the order of the different organs with respect to their phosphorus content relative to their fresh weight is the same, and this indicates that this content is proportional to the physiological activity. W. G.

The Application of Calorimetry to the Measurement of the Work of the Kidneys. FRANZ TANGL (*Biochem. Zeitsch.*, 1913, **53**, 36—40).—The energy metabolism of the kidneys was estimated by determining the heat production of rats placed in a calorimeter both before and after the extirpation of the kidneys. This was found to amount to 8·2% of the whole energy production of the body, and about 0·75 cal. per gram of kidney. This is the same as that found in the dog. Direct calorimetric measurements yield the same results as those obtained by Barcroft's method in the

analysis of the blood gases, and the author's own methods in the measurement of respiratory exchanges in curarised animals.

<div align="right">S. B. S.</div>

The Magnitude of the Work of Diseased Kidneys. STEPHAN CSERNA and G. KELEMEN (*Biochem. Zeitsch.*, 1913, **53**, 41—68).—The respiratory method of Tangl was employed in these researches, the respiratory exchanges of the animal being measured both before and after extirpation of these organs in animals which had been treated with renal poisons. These results were compared with those obtained in the normal (unpoisoned) animals. Dogs were used in the experiments, and the following poisons were employed: uranyl acetate, potassium cantharidate, potassium dichromate. Experiments were also carried out on animals, in which the blood-supply to the kidneys had been ligatured. It was found that the work of the diseased kidneys was greater than that of healthy ones, the oxygen consumption and carbon dioxide production both being larger. Only when the poison had been sufficiently powerful to produce anuria were these factors below normal. When the kidney work is increased, both the absolute and relative carbon dioxide production is greater than normal in diseased kidneys. By injury to the parenchyma of the kidney tissue produced by the stoppage of the circulation, the gaseous metabolism in the other organs is also increased.

<div align="right">S. B. S.</div>

The Magnitude of the Work of the Spleen. FRITZ VERZÁR (*Biochem. Zeitsch*, 1913, **53**, 69—79).—No alteration can be detected with certainty in the respiratory exchange after extirpation of the spleen of curarised dogs. By the direct measurement of the gaseous exchange in the blood passing through the spleen of cats by Barcroft's method, the oxygen consumption was found to be 0·05 c.c. of oxygen per gram per minute. This is about the same as that of the resting submaxillary gland or anuric kidneys, according to the researches of Barcroft. Dextrose, intravenously injected, and soluble starch are readily burnt up in the body, even after extirpation of the spleen.

<div align="right">S. B. S.</div>

The Changes in the Chemical Constitution of the Animal Body After Extirpation of the Spleen, Testis, and Thyroid. KARL DROGE (*Pflüger's Archiv*, 1913, **152**, 437—477).—The experiments were performed on dogs during the suckling period. Extirpation of the spleen delays growth, but whether this is the result of removing the organ or of the operation of laparotomy is uncertain. An increase of total ash (especially in calcium and to a smaller degree in phosphoric acid) was the only chemical change in the body noted. Extirpation of the thyroid does not affect growth, and causes a decrease in total ash. Extirpation of the testis does not affect growth, and a small decrease in the phosphoric acid of the ash occurs. Water, fat, fat- and ash-free substance, and proteins are not affected in all these classes of experiments.

<div align="right">W. D. H.</div>

Muscle Chemistry. IV (Addendum). The Muscle Tissues of some Sea Animals when Dried by Heat. GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem*, 1913, **86**, 137—140. Compare this vol., i, 219).—When dried at 100—102°, the muscle tissues of some sea animals lose substances having an alkaline reaction, produced by the decomposition of extractive substances. At a temperature of 110—112°, acid substances are lost.

In the case of *Scyllium catulus* it was found that the loss is chiefly to be attributed to ammonia, produced by the decomposition of carbamide.   N. H. J. M.

Catalase in Frogs' Muscles. EINAR HAMMERSTEN (*Chem. Zentr.*, 1913, i, 2051; from *Skand. Arch. Physiol.*, 1913, **29**, 46—59).— The action of a number of products of normal metabolism on the system catalase-hydrogen peroxide is investigated in a specially devised apparatus, frogs' muscles being used as the source of enzyme (compare Santesson, A., 1908, ii, 1061; 1910, ii, 331). The addition of creatinine causes a rapid increase in the rate of action at first; subsequently it falls owing to the using up of the peroxide. Creatinine decreases the rate of change similarly to Siegfried's "phosphor-meat acid." Choline hydrochloride and muscarine platinichloride have a direct harmful action on the enzyme. Acetaldehyde likewise lowers the activity, but reacts with hydrogen peroxide, fixing oxygen. Carhamide and alcohol are without effect. The muscle enzyme was more active in July and August than during December to June. When several substances act at once on the enzyme, the rate of change curves lie between those of the several constituents.   E. F. A.

Influence of Various Substances on the Gaseous Interchange of Surviving Frog's Muscle. XI. Action of Aromatic and Other Cyclic Compounds. TORSTEN THUNBERG (*Chem. Zentr.*, 1913, i, 2051; from *Skand. Arch. Physiol.*, 1913, **29**, 1—28. Compare A., 1911, ii, 56, 627).—The behaviour of a number of benzene derivatives on the gas exchange of surviving muscles is described. Monobasic carboxylic acids, such as benzoic acid and the toluic acids, lessen the exchange; hippuric acid behaves similarly, but is weaker. The introduction of a second carboxyl group overpowers the adverse influence of the first. Phthalic acid is hardly poisonous, isophthalic and terephthalic acids are slightly more so, and mellitic acid is very slightly poisonous. β-Phenylpropionic acid is as poisonous as phenylacetic acid. When the carboxyl group is in an unsaturated side-chain, the adverse effect on the exchange is much increased; this is exemplified by the behaviour of cinnamic, *allo*cinnamic, β-benzylidenepropionic, phenylpropiolic, and phenylmalonic acids. The salicylic acid grouping is more poisonous than the benzoic acid grouping. The para-compound is the least poisonous of the three hydroxytoluic acids. Anisic acid as a methoxy-compound is less poisonous than *p*-hydroxybenzoic acid. The presence of several hydroxy-groups does not greatly alter the action of the aromatic acids. The phenol-alcoholic acids, for

example, mandelic and phenylparaconic acids, are almost without effect.

Phenols are less poisonous than benzoic acid. It is considered that the benzene ring as such has a poisonous action on certain constituents of the cell concerned in the normal respiratory process. Nitration, as in mono- and di-nitrobenzoic acids, has little effect on the physiological action; sulphonation lessens the poisonous character of the ring. On the other hand, the hydrated six-membered ring in inositol and camphoric acid is inactive. The introduction of nitrogen into the ring, as in picolinic, nicotinic, and quinolinic acids, also counteracts the poisonous effect. Quinoline, which contains both pyridine and benzene nuclei, is strongly poisonous. Five-ring compounds are moderately poisonous.

E. F. A.

Organic Bases in the Roe of Herrings. KIYOHISA YOSHIMURA (*Zeitsch. physiol. Chem.*, 1913, **86**, 174—177).—The dry matter (92·093%) of the herring roe had the following composition: total N, 12·063; crude fat, 1·253; total P, 0·602; P as lecithin, 0·200; N as proteins, 0·601; N as ammonia and amines, 0·338; N as bases, 0·244%. One kilo. of the dried substance yielded 0·12 gram of trimethylamine, 0·02 gram of tetramethylenediamine, and 0·70 gram of choline.

N. H. J. M.

The Occurrence of Free Sulphuric Acid in the Mantle of Ascidia mentula. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1913, **86**, 345—346).—The cellulose mantle of *A. mentula* is acid, and this is due to sulphuric acid in the "bladder cells" of the mantle. Whether this is related to the acid cells of the blood is uncertain, for in *Phallusia mamillata*, although the blood-cells are acid, there is no acid in the mantle. There is less total sulphate in the expressed juice of *Phallusia* mantle than in the sea-water. The amount of chlorides in the two is equal.

W. D. H.

Presence of Carbamide in the Invertebrates and in their Excretion Products. ROBERT FOSSE (*Compt. rend.*, 1913, **157**, 151—154. Compare A., 1912, ii, 1203; this vol., i, 327, 432).—The author has proved the presence of carbamide in numerous invertebrates and their excretion products, and also in the water inhabited by them for any length of time, as follows:

Coelenterata: Actinia, and its products of excretion.

Echinoderm: Starfish, and products of excretion.

Worms: Sangsue officinale, cellular juice, and products of excretion.

Crustaceæ: Crayfish, cellular juice of the entire animal, of the flesh deprived of the organs, and of the liver; also in the products of excretion; spiny lobster, cellular juice, and excretion products; shrimp, cellular juice.

Insects: Silkworm, cellular juice; ant, eggs; fly, eggs.

Molluscs: Snail, entire animal, products of secretion and excretion; mussel, liquid in the shells; oyster, liquid in the shells.

W. G

The Mechanism of the Physiological Production of Light; Luciferase, Luciferin, and Luciferesceine. RAPHAEL DUBOIS (*Eighth Inter. Cong. App. Chem.*, 1912, 19, 83—89).—Phosphorescence in organisms is due, according to the author, to the interaction of two substances, which he has isolated more especially from the molluscular lamellibranch, *Pholades dactylus*. One of the substances, to which the name *luciferin* is given, can be extracted from the secreting organs by water, after heating to 70°, at which temperature it is stable. The other substance, *luciferase*, is, however, destroyed at 60°. By the action of one on the other in the presence of air, a phosphorescence is produced. The luciferase is of ferment-like character (oxydase), and it can be replaced by an oxidising agent, such as potassium permanganate, and by the blood of various cold-blooded animals, such as molluscs and marine crustaceans. Solutions of both substances give protein reactions, and the luciferin contains phosphorus and can be precipitated by picric acid. The term luciferesceine is adopted for the fluorescent substances in other animals, such as the fire-fly (compare McDermott, A., 1911, i, 396). S. B. S.

Indian Edible Swallows' Nests. HEINRICH ZELLER (*Zeitsch. physiol. Chem.*, 1913, 86, 85—106).—The substance, dried in a vacuum, contained 9·43% of total nitrogen, 1·35% of histidine, 1·20% of arginine, and 1·18% of lysine. When hydrolysed with 4% sulphuric acid, two reducing substances, not identified, were obtained. N. H. J. M.

The Ferments of the Milk Glands and of Milk. WALTHER GRIMMER (*Biochem. Zeitsch.*, 1913, 53, 429—473).—Both in resting and active milk glands proteoclastic ferments are present, which can digest the proteins of the glands themselves, but not other proteins, such as fibrin, gelatin, egg-white. Glycine, leucine, and other products of hydrolysis were formed. Tryptophan was found as hydrolysis product of the active, but not of the resting gland. The expressed juices, saline extracts, and autolysates of both resting and acting glands contain a peptoclastic ferment, which can set free tyrosine from milk peptone. Reasons are given for supposing that the peptoclastic and proteoclastic ferment are not identical. The active and resting glands contain a monobutyrinase, the activity of which is considerably weakened by dialysis. The milk glands of the ox and pig possess an amylolytic ferment both when active and resting. In the case of the cow, the amylolytic ferment is more active in the resting than in the active gland, whereas the resting glands of sheep possess no marked amylolytic capacity. All glands (expressed juices and saline extract) possess a ferment capable of hydrolysing salol, and it is shown that this action is not due to the alkalinity of the medium. A guaiacum peroxydase was only found in the lactating glands of ruminants. This is apparently not identical with the *p*-phenylenediamine oxydase, as no parallelism was found between the two ferments in the various glands, etc., investigated. S. B. S.

The Quantity of Alcohol Excreted by the Animal Organism Under Various Conditions. IV. The Influence of Dose and External Temperature on the Excretion of Alcohol by the Urine and Expired Air; the Absorption of Alcohol from the Urinary Bladder. WILHELM VÓLTZ and AUGUST BAUDREXEL (*Pflüger's Archiv*, 1913, **152**, 567—578. Compare A., 1912, ii, 466).—In doses of 3 c.c. of alcohol per kilo. of body weight in dogs, from 92 to 98% is oxidised in the body; at a low external temperature the figure is higher (96% at 16°, and 92% at 26°). A certain amount of alcohol is absorbed from the bladder when the concentration in the urine is not greater than the quantity found there after its ingestion.   W. D. H.

Respiration and Metabolism in Cardio-renal Disease. THOMAS LEWIS, JOHN H. RYFFEL, CHARLES G. L. WOLF, T. COTTON, G. L. EVANS, and JOSEPH BARCROFT (*Proc. physiol. Soc.*, 1913, liii—liv; *J. Physiol.*, **46**).—The fundamental factor in such cases is an increase in the proportion of acids (exclusive of carbon dioxide) in the blood. There is a fall in the alveolar carbon dioxide, and meionexy.   W. D. H.

The Combustion of Sugar in Pancreas Diabetes. FRITZ VERZÁR and A. VON FEJÉR (*Biochem. Zeitsch.*, 1913, **53**, 140—167).—Experiments were carried out on curarised tracheotomised dogs, with the object of ascertaining whether, after extirpation of the pancreas, the intravenous injection of sugar still caused a rise in the respiratory quotient, which serves as an indication that the sugar is being burnt in the body. Such a rise occurred up to the fourth day after the operation, after which no sugar was burnt up. In certain cases, when the animal is thus rendered diabetic, sugar injection causes a rise in oxygen consumption, but in others it does not. Neither by blood transfusion from another animal, nor by infusion of ordinary blood or of blood from the pancreas, could a rise in the respiratory quotient after sugar injection be brought about in depancreatised dogs; nor could any constant changes in this factor be produced by the pancreatic hormone of Knowlton and Starling.   S. B. S.

Blood-Dissociation Curves in Uræmia. EDWARD P. POULTON and JOHN H. RYFFEL (*Proc. physiol. Soc.*, 1913, xlvii—xlviii; *J. Physiol.*, **46**).—Four cases of uræmia were investigated; the alveolar carbon dioxide pressure is low (14 to 25 instead of 40 mm.), and the blood takes up oxygen with difficulty, so that the percentage saturation is from 37 to 43 instead of 52 to 63. The lactic acid of the blood was not increased except in one case. The urea in the blood was high in all (0·21 to 0·36 instead of 0·03%). The meionexy is not due to the urea; addition of urea to normal blood does not cause the shifting of the curve.   W. D. H.

The Influence of Hydroxyl and Carboxyl Groups on the Pharmacological Action of Nitric Esters. CHARLES R. MARSHALL (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 211—215).—The experiments were carried out on cats and rabbits with the following

substances: glycerol dinitrate, glyceryl methyl ether dinitrate, mannitol tetramethyl ether dinitrate, mannitol dimethyl ether tetranitrate, mannitol pentanitrate, dulcitol pentanitrate, and the nitric esters of tartaric, citric, and lactic acids, and of their ethyl ethers. It was found generally that the presence of hydroxyl or methoxyl groups considerably diminishes the vaso-dilating action of the nitric esters. When compared with completely nitrated alcohols containing the same number of nitro-groups, most (but not all) of the esters containing hydroxyl or methoxyl groups are much less active. Carboxyl groups diminish the vaso-dilating power even more than these, and the nitric esters of tartaric, citric, and lactic acids, after neutralisation with sodium carbonate, were completely inactive as vaso-dilators. S. B. S.

The Biological Behaviour of 6-Chloro m-hydroxytoluic Acid. ERNST SIEBURG (*Biochem. Zeitsch.*, 1913, **53**, 259—264).—The substance investigated [Me: OH: CO₂H: Cl=1: 3: 4: 6] acts antiseptically about six times more strongly than phenol, and thirty times more strongly than sodium salicylate. Kobert's method was employed, in which milk is mixed with sulphur, and the concentration of the drug just necessary to inhibit hydrogen sulphide formation was ascertained. Its antiseptic power was also confirmed when pure cultures in sterile human urine were employed. When administered to man, the acid is relatively non-toxic, and 2 grams can be tolerated when administered in one dose, without evil effects. It is excreted in the form of the sulphuric acid ester, which is crystalline, melts and decomposes above 200°, and can be synthetically prepared by Baumann's method, the synthetical substance and the substance isolated from urine after ingestion of the acid being identical. The acetyl ester is readily hydrolysed by ferments contained in beer-yeast, trypsin, taka-diastase, rabbit's pancreas, and rabbit's liver. S B. S.

[Pharmacological] Investigation of Two Bromo substituted Acidylcarbamides: Bromural and Adaline. Y. AIRILA (*Chem. Zentr.*, 1913, i, 2055; from *Skand. Arch. Physiol.*, 1913, **28**, 193 -277).—The pharmacological behaviour of bromural (monobromoisovalerylcarbamide), CHMe₂·CHBr·CO·NH·CO·NH₂, and of adaline (α-bromo-α-ethylbutyrylcarbamide),

$$CBrEt_2·CO·NH·CO·NH_2,$$

has been investigated. In rabbits both behave similarly, adaline being the more lethal; they cause a diminution in the blood pressure, but are without effect on the heart. E. F. A.

Action of Adrenaline on the Bronchioles. FREDERICK L. GOLLA and W. LEGGE SYMES (*Proc. physiol. Soc.*, 1913, xxxviii—xxxix; *J. Physiol*, 46).—In cat and rabbit, adrenaline causes constriction of the bronchioles, but after constriction has been established by other drugs, such as curare or muscarine, adrenaline then causes dilatation. The following drugs resemble adrenaline in this particular: epinine (3: 4-dihydroxyphenylmethylethylamine), tyramine (*p*-hydroxyphenylethylamine), methyl-

amine, ethylamine, and *iso*amylamine. Ergamine (β-amino-4-ethylglyoxaline) never produces bronchial dilatation.

W. D. H.

The Pharmacological Action of Bromostrychnines. CHARLES R. MARSHALL (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 217—223).—The two monobromostrychnines act like strychnine, but are eight to nine times weaker. Dibromostrychnine, although it still possesses a slight convulsant action in frogs and rabbits, produces in the former animals chiefly a paralytic effect, mainly due to a depression of the motor nerve-endings.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Favourable Action Exercised by Manganese on Acetic Fermentation. GABRIEL BERTRAND and ROBERT SAZERAC (*Compt. rend.*, 1913, **157**, 149—151).—The addition of minute quantities of manganese has a marked accelerating influence on the conversion of alcohol into acetic acid by *B. aceti*. At first the acceleration increases with the proportion of manganese, then it reaches a maximum, and begins to decrease. Under the experimental conditions stated, 1 part of manganese sulphate in 10,000 had the optimum effect.

W. G.

The Production of Acetaldehyde During the Anaerobic Fermentations of Dextrose by Bacillus coli communis (Escherich). EGERTON CHARLES GREY (*Biochem. J.*, 1913, **7**, 359—363). —By artificial selection of this bacillus by means of growth on sodium chloroacetate, strains have been obtained which produce little or no acetaldehyde. The formation of this product by the ordinary bacillus is related to the formation of alcohol, carbon dioxide, and hydrogen rather than to the other products. It is suggested that acetaldehyde is a primary product of the fermentation.

W. D. H.

Products of the Lactic Fermentation of Sugars. ALAN A. CLAFLIN (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 343—345).—There are considerable discrepancies between the statements of different authors with reference to the amount of lactic acid produced by the lactic fermentation of sugars, but the statement of Mayer and of Kayser is usually accepted, that the yield is not over 84%, and that considerable quantities of volatile acids are formed.

A further study of this question has shown that maltose, hydrolysed starch, and inverted sucrose give identical results when fermented with the same bacteria under the same conditions. It has been found that 95—97% of the sugar may be converted into

lactic acid with formation of not more than 0·5% of volatile acids, the balance consisting of unfermented sugars. If all the sugar is fermented, the yield of lactic acid is reduced to 90%, and that of the volatile acids increased to 5%, the balance probably disappearing as water and carbon dioxide. The volatile acids are formic, acetic, propionic, and butyric acids, acetic and butyric being present in the largest quantities. The formic acid does not amount to more than 1% of the original sugar. The propionic acid occurs in the proportion of one part to ten parts of acetic acid. The percentage of acetic acid depends on the degree of aeration, and may attain to as much as 30 parts to 70 parts of lactic acid.   E. G.

Influence of Some Colloids on Alcoholic Fermentation NICOLAAS L. SOHNGEN (*Chem. Zentr*, 1913, i, 2167—2168; from *Folia Microbiol., Holland. Bettr. gesamt. Microbiol*, 2).—Fermentation was effected between 38° and 40°, at which temperature the yeast no longer grows, but the fermentative function remains unchanged. The influence of a number of colloids on the process of alcoholic fermentation was investigated. Alkali humates have an adverse action. Colloidal iron, aluminium, or silicon oxides and humic acid have no measurable influence. Biocolloids, such as turf, bloodcharcoal, garden soil, have a markedly favourable action. This is attributed to the low concentration of carbon dioxide in these liquids, which favours the rapid formation and dissipation of bubbles, so that the medium does not become supersaturated. The aggregation of the gas bubbles at the colloidal surfaces accelerates their liberation and escape.   E. F. A.

Catalysts of Alcoholic Fermentation. HANS EULER and HENRY CASSEL (*Zeitsch. physiol. Chem*, 1913, 86, 122—129).—Whilst most of the substances known to accelerate fermentation have a comparatively slight effect—the maximum rarely exceeding 20%—it was found that addition of 0·04 gram of ammonium formate to 110 c.c. of water and 2 grams of sucrose resulted in an increase of 75%. Dry yeast was scarcely, if at all, influenced by ammonium formate.

Further experiments showed that the addition of ammonium formate affects the first phase of fermentation, in which an intermediate product, or products, are formed, more than the second phase (production of alcohol and carbon dioxide).

The effect of a given amount of organic salt is greater the less yeast is present.   N. H. J. M.

Influence of the Yeasts and of the Initial Constitution of the Musts on the Acidity of Fermented Liquids. JULES VENTRE (*Compt. rend*, 1913, 157, 154—156. Compare Fernbach. this vol., i, 231).—A study of the fermentation of sugar solutions by different yeasts in media of varying acidity, and of the effect of using different organic acids to produce the initial acidity. Each yeast produces a definite fixed and volatile acidity, the acidity increasing in neutral media, but diminishing in natural or artificial acid

media. Tartaric acid is preserved unchanged in original amount, but little being consumed by the different yeasts. Malic acid appears to be the most readily attacked by the yeasts. Each yeast has a power peculiar to itself of producing succinic acid.   W. G.

Fermentations with Yeast in Absence of Sugar. XII. Changes During Fermentation by Yeast. CARL NEUBERG and JOHANNES KERB (*Ber.*, 1913, **46**, 2225—2228; *Biochem. Zeitsch.*, 1913, **53**, 406—419).—Pyruvic acid, $CH_3 \cdot CO \cdot CO_2H$, is rapidly broken down by an enzyme in yeast into acetaldehyde and carbon dioxide (compare Neuberg and Kerb, A., 1912, ii, 973). The fermentation of a mixture of pyruvic acid and glycerol has been repeated on a large scale, using 100 litres of 1% pyruvic acid. Precautions were taken that the yeast had a high fermentative power, and allowance was made for the alcohol already present in the yeast used, and also for the alcohol formed by autofermentation. A considerable amount of alcohol is formed from pyruvic acid, and still more when both pyruvic acid and glycerol are present. It is considered that the influence of the glycerol is only indirect, in that it acts to protect the enzyme and increase its reducing power.

*iso*Butaldehyde and valeraldehyde are readily converted by yeast into the corresponding alcohols with a yield of 85% in the latter instance.   E. F. A.

The Separation of Life and Fermentative Power. THOMAS BOKORNY (*Pflüger's Archiv*, 1913, **152**, 365—436).—Experiments on yeast show that by chemical reagents of appropriate strength it is possible to kill the cells, but leave the enzymic power intact; for instance, this is accomplished by sulphuric acid from 0·1 to 0·5% concentration. Details regarding a large number of chemical reagents (inorganic and organic) are given. The kind of yeast used is one factor in the process.   W. D. H.

The Fat of Yeast. H. A. D. NEVILLE (*Biochem. J.*, 1913, **7**, 341—348).—The chief saturated acid in the fat of yeast is penta-decoic acid (Hinsberg and Roos, A., 1903, i, 56); arachidic acid and unsaturated acids with the formulæ $C_{16}H_{30}O_4$, $C_{18}H_{34}O_2$, and $C_{18}H_{32}O_2$ are also present. The cholesterol melts at 115 - 147°.
     W. D. H.

The Protein Substances of Yeast and their Products of Hydrolysis. PIERRE THOMAS and (Mme.) SOPHIE KOLODZIEJSKA (*Compt. rend.*, 1913, **157**, 243—246. Compare this vol., i, 912).— The authors have studied the products of hydrolysis of the two protein substances obtained from yeast (compare *loc. cit.*), one of which belongs to the casein group, and the other to the vegetable albumins. By hydrolysis with concentrated hydrochloric acid, followed by distillation with magnesium oxide, and then precipi-tation of the humic nitrogen by evaporation in acid solution, and of the amino-compounds with phosphotungstic acid, the nitrogen content has been determined as ammoniacal, humic, diamino· and

monamino-nitrogen.   The figures are in fairly close agreement with Osborne's values for casein.   Similar treatment of the cerevisine or vegetable albumin gives values agreeing well with Osborne's results for legumeline.

Hydrolyses have also been performed with sulphuric acid, and estimations made of the histidine, arginine, and lysine.   W. G.

A Forgotten Investigator.   A Contribution to the History of the Yeast Manufacture.   F. G. WALLER (*Chem. Weekblad*, 1913, **10**, 635—644).—A review of the development of the manufacture of yeast, in which the author contends that a practical technical method for its production by the air process was first devised by Eusebius Bruun.   A. J. W.

Potassium, Sulphur, and Magnesium in the Metabolism of Aspergillus niger.   H. J. WATERMAN (*Proc. K. Akad. Wetensch, Amsterdam*, 1913, **15**, 1349—1355).—Deficiency of potassium chloride allows the production of mycelium, but not of spore formation. Only in the concentration of $M/37,500$ does spore formation commence after eight days.   When potassium sulphate is added, larger quantities inhibit the formation of spore, which develop after two days, when potassium sulphate is absent.   After forty days, all the moulds were covered with spores in all the concentrations of sulphate added.   During the growth, sulphur accumulates in the cells, and is afterwards partly excreted.   Relatively large quantities of magnesium are necessary to produce a perceptible growth of mycelium, as none visible to the naked eye appeared even in the concentration of $M/2,470,000\text{-}MgSO_4,7H_2O$ per litre.   In the concentration $2M/247,000$, considerable growth only appeared after some days.   S. B. S.

Amygdalase and Amygdalinase in Aspergillus niger and Some Allied Hyphomycetes.   MAURICE JAVILLIER and (Mme.) HÉLÈNE TSCHERNORUTZKY (*Ann. Inst. Pasteur*, 1913, **27**, 440—449).—*Sterigmatocystis nigra* and most of the mosses examined contain unequal amounts of amygdalase and amygdalinase.   The amounts of both diastases is diminished in absence of zinc.   The diastases are active in solutions which are neutral or slightly acid to helianthin, and the optimum temperature is higher than that of the same diastases of almonds.

The percentage amount of the diastases in the plants varies with the age of the mycelium, and reaches its maximum at the time of sporulation.   The two diastases pass into the culture medium very unequally.   N. H. J. M.

Biological and Toxicological Studies on Penicillium stoloniferum (Thom.).   CARL L. ALSBERG and OTIS F. BLACK (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 15—23).—Cultures of *Penicillium stoloniferum* were obtained by Thom from spoiled Italian maize.   When grown on Raulin's medium, these were found to produce an acid, $C_{17}H_{20}O_6$, white needles, m. p. 140°, which was of phenolic character, almost insoluble in water, but soluble in

most organic solvents, to which the name *mycophenolic acid* is given. It gives with ferric chloride the colour which is character-istic of spoiled Italian maize, and resembles in many respects the lichen acids.   S. B. S.

Sterigmatocystis nigra and Lactose. HENRI BIERRY and (Mlle) F. COUPIN (*Compt. rend*, 1913, **157**, 246—247).—By cultivation of *Sterigmatocystis nigra* on Raulin's liquid for three days, then on a similar liquid deprived of all carbohydrate, and finally on this liquid with the sucrose replaced by lactose, lactase is produced in the plant, but in an endocellular form, and in con-sequence it does not pass into water when the crop is macerated with it.   W. G.

The Influence of the Chemical Constitution of Certain Organic Hydroxyl and Aminic Derivatives on their Germicidal Power. GILBERT T. MORGAN and E. ASHLEY COOPER (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 243—257).—The antiseptic value of several series of substances was investigated by Chick and Martin's modification of the Rideal-Walker process. The antiseptic value of the following classes of substances was ascertained. The aliphatic alcohols: The "carbolic acid coefficients" of these were all low. Certain phenols: The influence of the addition of alcohol to these was also investigated, and found to vary in different cases. The carbolic acid coefficients of the dihydroxybenzenes were as follows. (With *B. Typhosus*) Resorcinol, 0·29; catechol, 0·48; quinol, 1·1. The results with the nitrophenols were as follows (*Staphylococcus py. aur.*): *p*-Nitrophenol, 2·3; potassium *p*-nitrophenoxide, 0·52; *m*-nitrophenol, 3·5; picric acid, 7·5. The coefficients for coumarin, the coumaric acids and salts were low. The coefficients for the dihydroxynaphthalenes were, for the 2.3-derivative, 4·4, and for the 2:7-derivative, 2·8. The coefficients of several series of both aliphatic and aromatic amines were also determined. The chief results are the following (with *B. Typhosus*), ethylamine, 1·27; *iso*amylamine, 2·8; *n*-heptylamine, 24·3; *ac*-tetrahydro-β-naphthyl-amine, 5·3; aniline, 0·57; the toluidines, ortho-, 1·00; meta, 1·30; para-, 1·25; pyridine, 0·18.   S. B. S.

Compounds Obtained from Plant Seeds by the Methods for Extracting Lecithin. I. Introduction: Bean Seeds. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, **86**, 1—32).— A summary is given of previous work on plant phosphatides, and the opinion is expressed that the apparent differences between plant and animal phosphatides is due to the incomplete investigation of the former and to incorrect interpretation of the experimental results. The preparation and purification of the lecithin contained in *Phaseolus vulgaris* is described.   E. F. A.

Compounds Obtained from Plant Seeds by the Methods for Extracting Lecithin. II. Hydrolysis of Egg-albumin. III. Oat Seeds. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, **86**, 141—152, 153—173).—Previous experiments having shown that

aminoethyl alcohol is obtained by hydrolysing the lecithin of bean seeds, it became desirable to ascertain whether the compound could be obtained from other lecithins. Egg-lecithin, when hydrolysed, yielded, in addition to choline, small amounts of aminoethyl alcohol and glycerolphosphoric acid. Evidence was obtained that the aminoethyl alcohol is attached to the lecithin by the hydroxyl group, the amino-group being free.

Further experiments, with oats, showed that the phosphatides of the seeds of cereals are very similar to egg-lecithin and the lecithins of leguminous seeds. N. H. J. M.

Quantitative Experiments on the Effect of Formaldehyde on Living Plants. SARAH M. BAKER (*Ann. Bot.*, 1913, **27**, 411—442).—The results of experiments on the growth of seeds in atmospheres containing known amounts of formaldehyde showed that in presence of light, formaldehyde is utilised to some extent for the synthesis of food materials. In absence of light, formaldehyde is not assimilated; it seemed, however, to stimulate respiration.

Acetaldehyde is not assimilated in presence of light. The change in the dry weight of the cultures, when compared with the carbon dioxide respired, gave a ratio closely agreeing with that calculated for the complete oxidation of a carbohydrate. With cultures kept in darkness, no change occurred in the relations between loss in dry weight and the respired carbon dioxide. Formaldehyde was therefore not converted into carbon dioxide, and was not used as a source of food materials in absence of light.

It is probable that formaldehyde may function as a stage in photosynthesis; but the production of sugars and other food materials requires light energy. N. H. J. M.

Action of Sulphites, Thiosulphates, and Sulphur in Soils on the Growth of Plants. WALTER THALAU (*Landw. Versuchs-Stat.*, 1913, **82**, 161—209).—The results of pot experiments with different plants showed that, in a loamy soil, ammonium sulphite has the same effect as ammonium sulphate; in sand, ammonium sulphite has somewhat less effect than the sulphate; whilst in peat the yield was much less with sulphite.

In water cultures, ammonium sulphite is very injurious; germination is retarded in 0·4% solutions.

When exposed to air for a short time, ammonium sulphite is oxidised to sulphate; the rate of oxidation is increased by dissolving the salt in water, and still more in presence of soil.

Calcium sulphite was found to have no injurious action in loamy and sandy soils; in water cultures, and perhaps in peat, it reduced the yields. Sodium thiosulphate had no injurious effect. Flowers of sulphur had no very appreciable effect, and further experiments will be necessary. N. H. J. M.

Presence of Hemicelluloses in Root-stock, Rhizomes, and Tubers. ANTON STIEGER (*Zeitsch. physiol. Chem.*, 1913, **86**, 270—282).—The investigation of root-material from a number of

plants showed that in every case hemicellulose was present, a mixture of galactose and arabinose in approximately equal quantities being obtained on hydrolysis, whilst in no instance was either mannose or fructose present. The root and rhizome of *Asparagus officinalis* yielded only arabinose. The presence of much or little starch in the roots had no apparent effect. , It is left undecided whether the hemicelluloses act as a reserve or as a skeletal material in the vegetative parts of plants.   E. F. A.

Distribution of Asparagine, Glutamine, Arginine, and Allantoin in Plants. ANTON STIEGER (*Zeitsch. physiol. Chem.*, 1913, **86**, 245—269).—Asparagine and glutamine were sought for in the roots, underground shoots, portions above ground, or in the seedlings of a large variety of plants. It is characteristic of some families that they contain asparagine alone; in others only glutamine is present, whilst a few contain both amides. The last may contain either amide in excess or both in equal proportions. The results show a remarkable parallelism between the morphological-anatomical classification of the plants and their chemical behaviour. Certain irregularities are recorded where plants, in which normally only asparagine is present, sometimes contain more or less glutamine as well. Such variations are attributed to the altered conditions of environment.

Arginine almost always accompanies asparagine, but is less often present with glutamine. It is found when neither amide is present, where it probably acts as a reserve material.

The presence of allantoin in a number of plants is established.

E. F. A.

Antiaris Latex. HEINRICH KILIANI (*Ber.*, 1913, **46**, 2179—2188. Compare this vol., i, 381).—A fresh supply of preserved Antiaris latex was received from Mid-Borneo. It contained a deposit of, the protein in the form of well-defined, short columns. The latex is therefore a saturated solution of the protein, which must be a original ingredient, and not the product of subsequent fermentation. On this occasion, the most exhaustive extraction, full details of which are described, failed to yield more than one-sixth of the amount of glucosides which was previously obtained, and only β-antiarin (0·1% of the latex), but no α-antiarin could be isolated. The crude glucoside contained, however, a new active substance, which is easily soluble in water, and is designated *γ-antiarin*.

Ether extracted from the alcoholic solution of the glucosides a new *acid*, $C_{16}H_{14}O_7$ (?), which forms pale yellow, glistening crystals, sinters at 178—184°, is strongly acid, gives a *calcium* salt, and develops a green coloration with ferric chloride, changing to deep red with a drop of ammonia. The alkaline solutions rapidly darken in the air, from which it appears that the acid is a pyrogallol derivative, probably metameric with lecanoric acid.

J. C. W.

Alcohol From the Fruit of Arbutus unedo (Ellerone).
GIOVANNI SANI (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 884—885).—
Fermentation of this fruit yields a product containing 9·15—9·75%
of alcohol. The alcohol recovered from it by distillation had an
acidity of 0·132 gram per litre (as acetic acid), contained esters
(1·757 grams per litre, as ethyl acetate), furfuraldehyde, methyl
alcohol, and fusel oil (2·321 grams per litre), but no free or combined
hydrogen cyanide.   R. V. S.

Chemical Examination of the Seeds of the Cacao Tree.
L. REUTTER (*Compt. rend.*, 1913, 156, 1842—1844).—Ground cocoa
beans were treated with steam at 110°, deprived of oil, and extracted
with warm dilute methyl alcohol. On spontaneous evaporation,
the reddish-violet solution deposits white, microscopic crystals,
m. p. 184—185°. This substance, termed *cacaorine*, $C_{16}H_{20}O_6N_3$,
yields a neutral solution in water, which is optically inactive. On
hydrolysis, it yields theobromine and a small quantity of a reddish-
brown precipitate.

The mother liquor from cacaorine, when further concentrated,
yields *cacao-red*, $C_{40}H_{60}O_{27}N$, reddish-violet leaflets, which slowly
oxidise on exposure to air, becoming brown. It is soluble in water
and in methyl alcohol. The aqueous solution is coloured yellowish-
brown by alkalis, bright red by acids. It reduces Fehling's
solution, but is optically inactive. When hydrolysed by dilute
sulphuric acid, it yields carbon dioxide, a dextrorotatory sugar,
and *cacao-brown*, $C_{76}H_{78}O_{34}N$.   H. W.

Ash of the Castor Bean. MARSTON LOVELL HAMLIN (*Biochem.
Bull.*, 1913, 2, 410—411).—The following were the results obtained :

	SiO₂.	CaO.	MgO.	P₂O₅.	Mn.	Total ash.
Per cent. in dry oil-free kernel...	0·04	0·28	1·51	3·52	0·00056	7·3
Per cent. in ash	0·5	3·9	20·7	48·2	0·0076	—

Schulze and Godet obtained the following figures from dry,
but not oil-free, kernels :

	CaO.	MgO.	P₂O₅.	Total ash.
Per cent. in dry substance ...	0·15	0·72	1·16	3·64
Per cent. in ash	4·0	19·8	31·9	—

W. D. H.

The Composition of Coffee Essence ; Presence of Pyridine.
GABRIEL BERTRAND and GUSTAVE WEISWEILLER (*Compt. rend.*, 1913,
157, 212—213).—The authors have proved the presence of pyridine
in the infusion of freshly roasted and ground coffee, by precipitation
with silicotungstic acid and subsequent preparation of its platini-
chloride. Pyridine is present to the extent of 200—250 mg. per
kilo. of freshly roasted coffee.   W. G.

**Nitrogenous Constituents of the Fungus, Cortinellus
shiitake (P. Henn.).** KIYOHISA YOSHIMURA and M. KANAI (*Zeitsch.
physiol. Chem.*, 1913, 86, 178—184).—The sample examined contained
87·355% of dry matter of the following composition :

Nitrogen.			Crude fat.	Ash.	P_2O_5.
Total.	As proteins.	As ammonia.			
3·993	2·406	0·085	0·641	5·781	0·804

The following substances were obtained from 2 kilos. of the air-dried fungus: adenine, 0·40; choline, 0·41; alanine, 1·60; leucine, 2·30; copper glutamate, 0·50; proline, 0·30; mannitol, 50·00 grams: also a trace of trimethylamine and a little phenylalanine.

<div align="right">N. H. J. M.</div>

Latex of Ficus coronata; an Incomplete Vegetable Pancreatic Juice Containing a Proteolytic Enzyme, but no Amylase. C. GERBER (*Compt. rend.*, 1913, **156**, 1917—1919. Compare A., 1911, ii, 647; 1912, ii, 801, 977).—The latex has no action on starch paste or soluble starch, and consequently contains no amylase. Judging from its action on egg-yolk, it contains a lipase twice as active as that in the latex of *Ficus carica* (*loc. cit.*), and slightly more resistant to the influence of heat and of acids. It also contains a very active proteolytic ferment, which from its activity in coagulating milk appears to be four times as active as the similar ferment in *Ficus carica* latex, and more resistant to heat than the latter. The rennet of *Ficus coronata* is affected by acids and salts in the same way as that of *Ficus carica*. The latex is like that of *Morus nigra*, an incomplete vegetable pancreatic juice, but differs from this in containing a rennet more active towards boiled than raw milk.

<div align="right">T. A. H.</div>

The Influence of the Carbonates of the Rare Earths (Cerium, Lanthanum, Yttrium) on Growth and Cell Division in Hyacinths. WILLIAM HOWEL EVANS (*Biochem. J.*, 1913, **7**, 349—355).—The concentration of the carbonates of the rare earths necessary to produce physiological effects is very small. Lanthanum and cerium are favourable to growth and cell-division; yttrium is unfavourable. The lanthanum ion has a special effect on the flower-stalk, causing an increase in length.

<div align="right">W. D. H.</div>

Value of Caoutchouc in Kickxia-elastica. DAVID SPENC and WILLIAM F. RUSSELL (*Kolloid. Zeitsch.*, 1913, **13**, 41—46) —The authors have worked up six specimens of indiarubber latex by different methods with the object of ascertaining whether the kickxia caoutchouc could be converted into a good commercial product. They conclude that when carefully worked, this substance, as far as its physical properties are concerned, gives a good caoutchouc, but as far as its composition and other properties are concerned, the kickxia latex is inferior to the Plantagen-Hevea latex.

<div align="right">J. F. S.</div>

Analyses of Some Wyoming Larkspurs. I. FREDERICK W. HEYL, F. E. HEPNER, and SYLVESTER K. LOY (*J. Amer. Chem. Soc.*, 1913, **35**, 880—885).—Analyses are given of the various parts of *Delphinium Nelsoni*, *Delphinium glaucum*, and *Delphinium geyeri*.

The leaves of all three varieties were found to contain d-mannitol, whilst the last variety is found to yield the highest proportion of mixed alkaloids. D. F. T.

Constituents of the Berries of Kuko (Lycium chinense). T. Furuya (*Chem. Zentr.*, 1913, i, 1823; from *Arb. Pharm. Inst. Univ. Berlin*, **9**, 117—120).—The berries of Kuko (*Lycium chinense*) yield 0·0912% of betaine. E. F. A.

Constituents of the Roots of Stemona sessilifolia. T. Furuya (*Chem. Zentr.*, 1913, i, 1823—1824: from *Arb. Pharm. Inst. Univ. Berlin*, **9**, 112—116).—The powdered roots contain an alkaloid *hodorine*, $C_{19}H_{31}O_5N$, which was not obtained crystalline. The *hydrobromide* forms a colourless, odourless, crystalline powder, m. p. 258—259°. The *hydrochloride* has m. p. 244—247° (decomp.). E. F. A.

Manketti Seed Oil. Hermann Thoms (*Chem. Zentr.*, 1913, i, 1823; from *Arb. Pharm. Inst. Univ. Berlin*, **9**, 225—227).— Manketti seeds yield a pale yellow oil of nutty odour and agreeable flavour. The oil becomes cloudy at $-2°$. It is optically inactive, and has the following constants: Saponification number, 195·2; Reichert-Meissl, 1·085; Polenske, 0·6; iodine number, 130·4; Hehner number, 98·5; m. p. of the fatty acids, 40°; iodine number of these, 140·7; acetyl number, 163·2. The crude oil consists of the above oil, a half solid fat, m. p. 33°, and a watery fluid. E. F. A.

"Tannin Masses" in the Persimmon Fruit. Ernest D. Clark (*Biochem. Bull.*, 1913, **2**, 412—418).—On hydrolysis of tannin masses from the persimmon, tannin, phloroglucinol, and much colloidal residue are obtained, but no hexose or pentose. The union between the two first-mentionel substances is probably similar to that of phloroglucintannoids in various plants. The colloidal residue is cellulose-like. In the presence of phloroglucinol, the ferric chloride test for tannin is untrustworthy. W. D. H.

Investigation of Puccinia graminis Persoon. A. von Pomarski (*Chem. Zentr.*, 1913, ii, 288; from *Sep. Zool. Lab.*, 1912, **8**, 85—120).—The air-dried spores of *Puccinia graminis* contain 12·1% of moisture, 3·25% of nitrogen, 5·1% of fat, and 9·15% of cell membrane. The last yields dextrose, formic and acetic acids on hydrolysis, it contains about 7% of nitrogen, and is analogous to chitin or chitosan.

The fat contains lauric acid, heptoic acid, oleic acid, and glycerol, also 32% of a wax and dioleinlecithin.

Dextrose, mannitol, and an unknown disaccharide are present, also the enzymes, invertase, catalase, diastase and lipase, as well as brownish-red and green pigments. E. F. A.

Arsenic and Manganese in Some Seaweeds. Henri Marcelet (*Chem. Zentr.*, 1913, ii, 278; from *Bull. Sci. Pharmacol.*, 1913, **20**, 271—275).—Seaweeds contain from 0·005 to 0·5 mg. of

arsenic per 100 grams of dry material. Apparently the proportion of arsenic is greatest when that of chlorophyll is least; this is the opposite of the relation in land plants. In *Posidonia* the leaves contain 0·045 mg.; the roots, 0·035 mg.; and the whole plant, 0·04 mg. of arsenic per 100 grams.   E. F. A.

Occurrence of Trehalose in Selaginella lepidophylla. OTTO ANSELMINO and E. GILG (*Ber. deut. Pharm. Ges.*, 1913, **23**, 326—330). —On extraction with alcohol, *Selaginella lepidophylla* furnished trehalose, which was identified by means of its melting point, composition, etc. *S. Galeottii* and *S. Kraussiana* yielded no trehalose.   T. A. H.

The Unsaponifiable Constituents of Sesame Oil. ALFRED HEIDUSCHKA (*Eighth Inter. Cong. App. Chem.*, 1912, **11**, 13—16).— Sesame oil contains three unsaponifiable substances, namely, phytosterol, sesamin, and a thick yellow oil. The phytosterol, m. p. 136·2—136·8°, is a definite compound, and cannot be separated, by fractional crystallisations, into fractions having different melting points. Sesame oil yields about 0·17% of sesamin; this contains 67·36% of carbon and 5·43% of hydrogen, and has a molecular weight of 341·8. From these figures the formula $C_{20}H_{19}O_6$ is deduced for the substance. The yellow oil could not be separated into any characteristic or definite substances.
                          W. P. S.

Chemical Examination of Wheat Germ. FREDERICK B. POWER and ARTHUR H. SALWAY (*Pharm. J.*, 1913, **91**, 117—120).— Wheat germ was found to contain sitosterol, choline, betaine, allantoin, sucrose, dextrose, and raffinose; no evidence was obtained of the presence of asparagine, which has been recorded as a constituent of wheat germ by Frankfurt (A., 1897, ii, 67). About 7% of fatty oil was obtained from the wheat germ under examination, the oil consisting of the glycerides of stearic, palmitic, and linolic acids; the quantity of linolic acid was about three times as much as that of the total solid acids. The amount of resinous substance present was 0·04%, as was also a small quantity of an amorphous glucosidic substance. It was ascertained that wheat germ contains a very small amount of sinapic acid, probably present as sinapine, a choline ester of sinapic acid.   W. P. S.

Influence of the Lime-Magnesia Ratio. P. L. GILE and C. N. AGETON (*J. Ind. Eng. Chem.*, 1913, **5**, 564—567).—Experiments are described in which bush beans were grown for three years on plots 30 × 60 dcm., the soil of which contained varying proportions of lime and magnesia.

The results indicate that bush beans are independent of lime-magnesia ratio in the soils employed; and that the amount of lime in the plants remained the same, with increasing amounts of lime in the soil.

The conclusion is drawn that whilst the ratios of different salts,

including lime and magnesia, affect plant growth under certain conditions, the hypothesis of the lime-magnesia ratio cannot be considered as applying to all soil conditions. N. H. J. M.

Unfermentable Sugar (Pentose) and the Formation of Furfuraldehyde in Wine. RUDOLF HAID (*Chem. Zentr.*, 1913, i, 2170; from *Zeitsch. Gärungsphysiol*, 1913, **2**, 107—109. Compare Pasquero and Cappa, A., 1912, ii, 103).—The furfuraldehyde formed on the distillation of wine cannot be derived from *l*-arabinose, since this pentose, when distilled with malic or tartaric acid, does not yield furfuraldehyde. An unknown pentose is assumed to be the source of the aldehyde. E. F. A.

The Advance and Prospects of the Newer Agricultural Chemistry (Chiefly Land Chemistry) since the Discoveries of Modern Physical Chemistry and Colloidal Chemistry Have been Employed. HANS BREHM (*Kolloid. Zeitsch*, 1913, **13**, 19—35).—The author considers the work which has been done in connexion with agricultural soil and the processes taking place in it, from the colloidal chemistry point of view. The various substances occurring in the soil are individually considered, and a long bibliography of the chief researches on the subject from 1901 to the present time is given. J. F. S.

Mineralogical Soil Analysis. WILLIAM J. McCAUGHEY (*J. Ind. Eng. Chem.*, 1913, **5**, 562—564).—The potassium minerals usually present in soils are orthoclase, microcline, muscovite, and biotite. Muscovite is the most resistant, and probably contributes very little to the soil solution; biotite is the most readily decomposed. Orthoclase is the commonest, and occurs in amounts varying from 3 to 30%.

The commonest calcium minerals are epidote, hornblende, plagioclase, and garnet. Epidote is a normal constituent of most soils, whilst garnet, which is formed by contact metamorphism, occurs less frequently. Hornblende is the common calcium mineral, and weathers generally, forming chlorite.

Quartz crystals occur so frequently in limestone soils and are so exceptional in others, that their presence seems to indicate origin from limestone. N. H. J. M.

Quantitative Investigations on the Reaction of Aqueous Extracts of Soils. TEODOR SAIDEL (*Bull. Acad. Sci. Roumaine*, 1913, **2**, 38—44).—An electrical method for estimating the reaction of soil extracts is described with sketch of the apparatus employed. The difficulty due to loss of carbon dioxide when hydrogen is passed through the solution can be overcome by mixing the hydrogen with a definite amount of carbon dioxide, or else by boiling off the carbon dioxide.

The results of estimations obtained with several soils shows that there is a considerable difference in reaction between forest soils and the soils of the steppes on the one hand, and podsol soils on the other. N. H. J. M.

Alkaline Reactions Caused by Acids and their Acid Salts in Soils. GIULIO MASONI (*Chem. Zentr.*, 1913, i, 1999 ; from *Staz. sperim. agrar. ital.*, 1912, **46**, 219—240. Compare A., 1912, ii, 677).— Organic and mineral acids and their acid salts are able to cause an alkaline reaction in soils. In calciferous soils, calcium carbonate is formed, which in aqueous solution, on the addition of acid, parts with hydroxyl. The alkaline reaction may also be due to the action of acids on basic salts of magnesium, calcium, or aluminium. Acid alkali salts will give rise to alkali carbonates. The influence of the alkaline reaction on the biological function of the roots is discussed.   E. F. A.

Behaviour of Amino-acids in the Soil. SAMUEL L. JODIDI (*Eighth Inter. Cong. App. Chem.*, 1912, **26**, 119—134. Compare A., 1911, ii, 820 ; 1912, ii, 292).—In connexion with a study of the proteins contained in soils, experiments have been undertaken to ascertain the rate at which amino-acids in the soil eliminate their nitrogen in the form of ammonia and whether the process is quantitative. In these experiments, definite quantities of various amino-acids were mixed thoroughly with weighed portions of soil and kept in covered vessels at 22—27° ; after the lapse of some days the quantity of ammoniacal nitrogen formed was estimated. The various amino-acids yielded under these conditions the following maximum proportions of ammonia: glycine, 81·03% ; alanine, 75·58% ; leucine, 59·62% ; aspartic acid, 72·74% ; glutamic acid, 72·19% ; phenylalanine, 54·31% tyrosine, 59·65% asparagine, 77·47%.

The results do not show whether amino-acids can be quantitatively de-aminated in the soil. It is possible that during the course of the process, some of the ammonia produced is oxidised to nitrites and nitrates. There are also other factors to be taken into consideration. It has been demonstrated, however, that the amino-acids examined readily lose nitrogen in the form of ammonia, and that the rate of the change is greatly influenced by the structure of the acids, acids of similar structure yielding about the same proportion of ammonia.   E. G.

Normal and Abnormal Constituents of Soil Organic Matter. ELBERT C. LATHROP (*Eighth Inter. Cong. App. Chem.*, 1912, **15**, 147—151).—The following compounds may be considered as normally present in soils : pentosans, pentoses, histidine, xanthine, hypoxanthine, cytosine, and, perhaps, creatinine. Arginine and adenine only occur infrequently, whilst dihydroxystearic and picolinecarboxylic acids, being injurious to plants, must be classed as abnormal soil constituents.

It is uncertain whether agroceric, lignoceric, paraffinic and mono-hydroxystearic acids, agrosterol, phytosterol, and hentriacontane should be considered as normal or abnormal constituents of soils.
                                                N. H. J. M.

Organic Chemistry.

Determination of the Critical Constants of Methane. ETTORE CARDOSO (*Arch. Sci. phys. nat.*, 1913, [iv], **36**, 97—100).—Preliminary details are given of the apparatus employed in the determination of critical constants; the following values are found for methane : critical temperature, 82·85° ; critical pressure, 45·60 atm. ; critical density, 0·1623. J. F. S.

Preparation of Erythrene and Isoprene. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 261876).—When the hydrochlorides of δ-dimethylamino-Δ*ᵅ-isoamylene* and of δ-dimethylamino-Δ*ᵅ*-butylene (this vol., i, 342) are heated at 200—240°, they decompose into dimethylamine and isoprene or erythrene respectively. F. M. G. M.

Preparation of Halogenated Propanes. HENDRIK JACOBUS PRINS (D.R.-P. 261689).—Compounds of general formulæ C_3X_7H, $C_3X_6H_2$ and $C_3X_5H_3$ (where X is Cl or Br), are readily prepared from a mixture of halogenated methane and halogenated ethylenes (of formulæ $CX_3 \cdot CHX$ and $CHX \cdot CHX$) by mixing together in the required proportions in the presence of aluminium chloride or bromide at about 20°.

aaaβγγ-Hexachloropropane, $CCl_3 \cdot CHCl \cdot CHCl_2$, obtained from chloroform (or carbon tetrachloride) and dichloroethylene, is a colourless liquid, b. p. 216° ; when treated with alcoholic potassium hydroxide at the ordinary temperature, it gives rise to *aaβγγ-pentachloropropylene*, $CCl_2 \cdot CCl \cdot CHCl_2$, b. p. 184°, from which *aββ-trichloroacraldehyde*, $CCl_2 \cdot CCl \cdot CHO$, b. p. 164°, is obtained by the action of concentrated sulphuric acid, which latter can further be converted into *aβ-dichloroacrylic acid*, $CHCl \cdot CCl \cdot CO_2H$, and its *amide*, $CHCl \cdot CCl \cdot CO \cdot NH_2$, m. p. 132°.

aaaβγγγ-Heptachloropropane, $CCl_3 \cdot CHCl \cdot CCl_3$, is an oil with a penetrating odour, m. p. 11—12°, b. p. 164—166°/90 mm., D^4 1·9, $n_D^{16·5}$ 1·5418, and in a similar manner furnishes *hexachloropropylene*, C_3Cl_6, b. p. 210°, and *trichloroacrylic acid*.

aaβγγ-Pentachloropropane, $CHCl_2 \cdot CHCl \cdot CHCl_2$, a colourless liquid, b. p. 198—200°, gives rise to *aβγγ-tetrachloropropylene*,
$$CHCl \cdot CCl \cdot CHCl_2,$$
b. p. 65°, and the *aldehyde*, $OH \cdot CH \cdot CCl \cdot CHO$, m. p. 145°.

aaβ-Pentabromopropane, $CHBr_2 \cdot CHBr \cdot CHBr_2$, has b. p. 163—165°/18 mm. F. M. G. M.

Catalytic Action of Certain Manganese Salts on Alcohols (Spirits) in the Presence of Hydrogen Peroxide. A. C. CHAUVIN (*Ann. Fal.*, 1913, **6**, 463—466).—The addition of 1% of hydrogen peroxide solution (perhydrol) to crude alcohol, spirits, and liqueurs, produces, after thirty days' contact, an increase in the quantities of the usual impurities (aldehydes, esters, higher alcohols, etc.), which were

present originally, but the furfuraldehyde tends to disappear. The action of the peroxide is augmented by the addition of about 0·01% of manganese salts, the acetate having the greatest effect. In the case of kirsch liqueur the hydrocyanic acid is decomposed by the treatment, whilst the essential oils present in absinthe are resinified. W. P. S.

Preparation of Esters from Alcohols and Organic Acids. OTTO HAUSER and ADOLF KLFOTZ (D.R.-P. 261878).—An account of work previously described (Hauser and Klotz, this vol., i, 246). tert.-*Butyl* n-*nonoate* has b. p. 242°, and tert.-*butyl* n-*octoate*, b. p. 231°.
F. M. G. M.

Alkylation of Ethyl Cyanoacetate. JOHN O. HESSLER (*J. Amer. Chem. Soc.*, 1913, 35, 990—994).—The ethylation of ethyl cyanoacetate has already been studied (Hessler, A., 1908, i, 182; 1904, i, 830; Hadley, A., 1912, i, 699), and the author has now turned his attention to the substitution of other alkyl groups into this ester.

Crude ethyl a-cyanopropionate, obtained by the action of sodium ethoxide and methyl iodide on an alcoholic solution of ethyl cyano-acetate (Henry, A., 1887, 796), after shaking with 10% sodium hydroxide solution and subsequent fractionation yielded about 12% of ethyl a-cyano-a-methylpropionate, b. p. 77°/9 mm., 185°/ord. pressure, D^{26} 0·971. The sodium hydroxide extract contained a-cyanopropionic acid, b. p. 142—145°/11 mm., D^{20} 1·14, from the silver salt of which pure ethyl a-cyanopropionate, b. p. 89—90°/20 mm., 192—193°/ord. pressure, D^{22} 0·998, was obtainable by the action of ethyl iodide.

Crude ethyl a-cyano*iso*valerate, prepared in a similar manner to the above methyl derivative, was submitted to like treatment with sodium hydroxide; it yielded about 10% of ethyl a-cyano-a-*iso*propyl-*iso*valerate, b. p. 240°, $D^{29·4}$ 0·918, and also cyano*iso*valeric acid, b. p. 166—168°/28 mm.; the silver salt of the latter reacted vigorously with ethyl iodide, giving pure ethyl a-cyano*iso*valerate, b. p. 113°/25 mm., 211°/739 mm., $D^{29·2}$ 0·962.

Crude ethyl a-cyano-a-*iso*heptoate contained 28% of ethyl a-cyano-a-*iso*amyl*iso*heptoate, b. p. 158—159°/16 mm., D^{22} 0·909, which was unaffected by long standing with cold 10% sodium hydroxide solution; the sodium hydroxide extract yielded a-cyano*iso*heptoic acid, m. p. 47—48°, which was converted through the ammonium salt into the silver salt; this reacts with ethyl iodide, giving ethyl a-cyano*iso*-a-heptoate, b. p. 125°/12 mm., 241°/749 mm., D^{21} 0·939, which is readily hydrolysed by 10% sodium hydroxide solution.

a-Cyano-a-*iso*heptoamide, m. p. 142°, obtained by the action of con-centrated ammonia solution on the ester, when heated in a vacuum with phosphorus pentachloride to 120—130° undergoes conversion into a-cyano-a-*iso*heptonitrile, b. p. 121—122°/18 mm., D^{25} 0·899.
D. F. T.

Glycerol Esters of Benzoic and Myristic Acids, and the Partial Saponification of Triglycerides. ANDREAS LIPP and P. MILLER (*J. pr. Chem.*, 1913, [ii], 88, 361—394).—The author reviews

previous work on the hydrolysis of fats, and points out that, although it is now generally accepted that the hydrolysis of triglycerides takes place in stages with the intermediate formation of diglycerides and monoglycerides, only in the case of sulphuric acid as a hydrolytic agent has this view been placed beyond all doubt by the isolation of the intermediate products (compare Thieme, A., 1912, i, 333; Grün and Corelli, *ibid.*, 409). The work described in the present paper deals with the hydrolysis of tribenzoin and trimyristin by means of water and alkali hydroxides in aqueous, alcoholic and acetone solutions. It is definitely proved by the isolation of the corresponding di- and mono-glycerides from the product obtained by partial saponification of the triglycerides, that in these cases also a similar hydrolysis in stages takes place.

When heated in sealed tubes at 225° in an atmosphere of carbon dioxide an equimolecular mixture of benzoic acid and glycerol yields as main product a-monobenzoin, which is freed from the accompanying aa-dibenzoin by taking advantage of its solubility in water; the latter compound forms the chief product if the benzoic acid is in excess (2 mols.).

In agreement with the observations of Thieme (A., 1912, i, 333) on the simultaneous formation of mono- and di-glycerides by the inter-action of the sodium salts of acids and glycerol a-monochlorohydrin, the authors find that the latter compound reacts at 175° with sodium benzoate, yielding a mixture of a-mono- and aa-dibenzoin.

Glycerol ay-dichlorohydrin and sodium benzoate at 190° give rise to a-monobenzoin, aa-dibenzoin, and tribenzoin. aa-Dibenzoin is an oil; the solid dibenzoin, described by Baumann (A., 1887, 229) and Grün (this vol., i, 157), probably consists of impure tribenzoin. The latter compound is obtained by shaking glycerol with benzoyl chloride (5 mols.) and aqueous sodium hydroxide at a low temperature. If less than this amount of benzoyl chloride is used, it is accompanied by varying amounts of mono- and di-benzoin (compare Baumann, *loc. cit.*, and Balbiano, A., 1903, i, 547).

The separation of mono-, di-, and tri-benzoin can be accomplished by taking advantage of the solubility of the monobenzoin in water and the greater solubility of the dibenzoin in alcohol as compared with that of the tribenzoin. When treated in alcoholic solution with 5% of the amount of potassium hydroxide, theoretically necessary for complete hydrolysis, and the mixture maintained for twenty-four hours at the ordinary temperature, tribenzoin undergoes complete decomposition into glycerol, ethyl benzoate, and potassium benzoate; if the reaction is allowed to proceed for only two minutes and the excess of potassium hydroxide at once neutralised by the addition of hydrochloric acid, then monobenzoin and dibenzoin are also formed.

The latter compounds were also isolated from the product obtained by partly hydrolysing the tribenzoin by means of potassium hydroxide in acetone at the ordinary temperature, and by heating with water in sealed tubes at 200°, both the water and potassium hydroxide being present in insufficient amount for complete hydrolysis. Partial saponification with 10% aqueous sodium hydroxide gave only di-

benzoin; the absence of the monobenzoin is referred to its solubility in water and consequent rapid hydrolysis by the sodium hydroxide.

When heated at 250° in sealed tubes in an atmosphere of carbon dioxide, a mixture of myristic acid and glycerol in equimolecular proportions yields trimyristin, αα-dimyristin and α-monomyristin, the latter compound forming the main product. The method adopted in separating the three compounds is based on the sparing solubility of the monomyristin in cold light·petroleum, and the greater solubility in alcohol of the dimyristin in comparison with that of the trimyristin. Monomyristin (Krafft, A., 1904, i, 136) has m. p. 68°; when heated to 70° and allowed to cool slowly it solidifies at 54°; if the temperature is allowed to fall to 44° and the substance again heated, it has m. p. 55°; on further heating it solidifies at about 60° and then shows the original m. p. of 68°.

αα-Dimyristin has m. p. 64·5° (compare Grün and Theimer, A., 1907, i, 463; also *ibid.*, 464, and this vol., i, 159). ·

Trimyristin exists in two forms of m. p. 56·5° and 49° (compare Reimer and Will, A., 1885, 1197).

The results obtained in the partial hydrolysis of trimyristin resemble those described above in the case of tribenzoin.   F. B.

The Glycerides of Butter Fat. CONRAD AMBERGER (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 65—85).—Glycerides of definite composition were isolated from butter fat by subjecting the latter to fractional solution and crystallisation in ether. The most insoluble glyceride was found to consist of tristearin in the case of some butters; with other butters it was palmityldistearin.

Stearyldipalmitin was also obtained from butter fat, proving the presence of stearic acid.   W. P. S.

Tripropionin. RUDOLF W. SEUFFERT (*Zeitsch. Biol.*, 1913, **61**, 551—553).—*Tripropionin* is readily obtained by the gradual addition of the calculated amount of propionic anhydride to glycerol heated at 150—165°. It has b. p. 177—182°/ca. 20 mm., n_D^{19} 1·43175. The compound is not formed by heating glycerol with propionic acid in the presence of sodium acetate, whilst, when propionyl chloride is employed under varying conditions, the product obtained invariably contains chlorine.   H. W.

Catalytic Decomposition of Esters of Dibasic Organic Acids by Alumina. LOUIS MICHIELS (*Bull. Soc. chim. Belg.*, 1913, **27**, 227—230).—Senderens (this vol., i, 342) has observed that ethylene, carbon dioxide, carbon monoxide, and hydrogen are formed by the decomposition of ethyl succinate in the presence of alumina at 390° and 420°, and has surmised that a diketone may also be formed under these conditions. The author has investigated this action at 260°. The main gaseous product is ethylene mixed with some carbon dioxide. The distillate consists almost entirely of succinic anhydride. Diketones or their condensation products are only present in very small quantity, since the crude distillate is almost completely soluble in alkalis.

Similarly, ethyl glutarate under the influence of alumina at 270° yields mainly ethylene and glutaric acid. In one experiment, ethyl hydrogen glutarate was also isolated. In like manner, ethyl adipate at 300—320° yields an acid distillate. The general course of the reactions is shown by the equation :

$$CO_2Et\cdot[CH_2]_x\cdot CO_2Et = CO_2H\cdot[CH_2]_x\cdot CO_2H + 2C_2H_4.$$
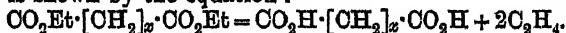
H. W.

The Nitrogenous Constituent of Kephalin. A. BAUMANN (*Biochem. Zeitsch.*, 1913, **54**, 30—39).—The kephalin was hydrolysed with dilute hydrochloric or sulphuric acid at 60°. From the aqueous solution, after separation of the insoluble products and the glycero-phosphates (by means of lead acetate), the salt of an organic base could be separated by means of alcohol, which contains the amino-groups pre-existent in kephalin. This could be identified by means of the auri- and platini-chlorides as hydroxyethylamine. S. B. S.

Catalytic Acceleration of the Absorption of Oxygen by Lecithin with Iron Salts. TORSTEN THUNBERG (*Zeitsch. physiol. Chem.*, 1913, **87**, 82); OTTO WARBURG (*Ibid.*, 83—84).—A claim for priority. Thunberg (A., 1910, ii, 323) had previously noticed that the oxidation of lecithin was accelerated by the presence of iron salts (compare Warburg and Meyerhof, this vol., i, 698). Thunberg also claims priority with reference to the influence of freezing and finely powdering the cells. Warburg denies this; he comes to precisely the opposite conclusions to Thunberg. E. F. A.

Preparation of Acetic Acid. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 261589).—The oxidation of acetaldehyde to acetic acid by air or oxygen proceeds satisfactorily at 70—100° or at lower temperatures (30—80°) in the presence of a catalyst, such as ferrous oxide, uranium oxide, acetic anhydride, or acetyl chloride.

F. M. G. M.

Decomposition of Trichloroacetic Acid by Mercuric Oxide. KURT BRAND (*J. pr. Chem.*, 1913, [ii], **88**, 342—357).—When mercuric oxide is added to a concentrated solution of trichloroacetic acid and the mixture heated to boiling, a vigorous reaction occurs, resulting in the formation of carbon monoxide, carbon dioxide, chloroform, hydrogen chloride, mercuric and mercurous chlorides ; at 60° the reaction proceeds according to the equation :

$$2CCl_3\cdot CO_2H + 5HgO = 4CO_2 + 4HgCl + HgCl_2 + H_2O.$$

The author considers that the mercuric trichloroacetate first produced decomposes into dichloromethylene, carbon dioxide, and mercuric chloride, thus : $Hg(CCl_3\cdot CO_2)_2 = 2CCl_2 + 2CO_2 + HgCl_2$, the dichloromethylene being converted by the action of water into dihydroxymethylene, which is transformed at 60° into formic acid, and at 100° into formic acid and carbon monoxide. The formic acid is then oxidised by the mercuric chloride to carbon dioxide. The formation of chloroform during the reaction is referred to the decomposition of free trichloroacetic acid, formed from the mercuric trichloroacetate, either by hydrolysis or by the action of hydrochloric acid. F. B.

Cholic Acid. III. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1913, **87**, 59—73. Compare A., 1910, i, 10 ; 1911, i, 10).—A re-investigation of cilianic acid and its methyl ester (compare Pregl, A., 1903, i, 318) establishes it as a tetrabasic acid, $C_{24}H_{34}O_{10}$ or $C_{24}H_{22}O_{10}$, the ester being a tetramethyl derivative. Cilianic acid is accordingly an oxidation and not a degradation product of cholic acid. The carbon dioxide formed during the oxidation is derived from the decomposition of part of the cilianic acid.   E. F. A.

Senecioic Acid. YASUHIKO ASAHINA (*Arch. Pharm.*, 1913, **251**, 355—356).—Senecioic acid, $C_5H_8O_2$, the unsaturated acid obtained from the rhizomes of *Ligularia tussilaginea* (*Senecio kaempferi*) is proved to be identical with $\beta\beta$-dimethylacrylic acid by the direct comparison of the two acids, m. p. 69—70°, and of their calcium salts, $(C_4H_7 \cdot CO_2)_2Ca, 4H_2O$.   C. S.

Action of Cyanides on Aldehydes and Ketones. HARTWIG FRANZEN and WALTER RYSER (*J. pr. Chem.*, 1913, [ii], **88**, 293—306). —It has been shown previously (A., 1909, i, 804) that ethyl acetoacetate, ethyl benzoylacetate, and acetylacetone, when shaken with aqueous solutions of calcium, barium, strontium, and magnesium cyanides, yield crystalline salts, which were considered to be metallic derivatives of cyanohydrins, having a similar structure to that of the calcium derivative of mandelonitrile, obtained by the action of calcium cyanide on benzaldehyde.

The authors now find that the products are not nitriles, but the metallic derivatives of the ketonic esters and diketone.

The preparation of the calcium, barium, strontium, and magnesium derivatives of ethyl acetoacetate, and the *calcium, strontium,* and *magnesium* derivatives of acetylacetone is described.

The metallic derivatives of ethyl benzoylacetate decompose very rapidly, and, therefore, could not be isolated in a pure condition.

The calcium derivative of mandelonitrile, $Ca(O \cdot CHPh \cdot CN)_2$, has been obtained in a state of purity by using an aqueous solution of calcium cyanide, prepared from calcium hydroxide and hydrocyanic acid, instead of the mixture of calcium chloride and potassium cyanide employed previously (*loc. cit.*). Its constitution has been established by its conversion into the benzoyl derivative of mandelonitrile by the action of benzoyl chloride.

The *calcium* derivative of *o*-chloromandelonitrile, prepared from *o*-chlorobenzaldehyde and aqueous calcium cyanide, forms a light yellow powder.

The *calcium* derivatives of *p*-methylmandelonitrile and *p*-methoxymandelonitrile are also described.

The colourless, crystalline substance obtained by Kohn (A., 1900, i, 205) by the action of calcium cyanide on formaldehyde in aqueous solution is considered to have the constitution

$$Ca[O \cdot CH(CN) \cdot Ca \cdot OH]_2.$$

Acetaldehyde yields a similar crystalline compound,

$$Ca[O \cdot CMe(CN) \cdot Ca \cdot OH]_2.$$

The action of potassium cyanide on acetaldehyde in aqueous solution results in the formation of alanine and α-iminodipropionic acid.

F. B.

The Action of Silicon Tetrachloride on Aldehydes and Ketones. JAMES N. CURRIE (*J. Amer. Chem. Soc.*, 1913, **35**, 1061).— It has been observed that a mixture of pure acetone with silicon tetrachloride in a few hours sets to a gelatinous mass, which when broken up with water gives a brown oil consisting mainly of mesityl oxide.

Analogous results were obtained in qualitative experiments with other aldehydes and ketones. D. F. T.

Photochemical Synthesis of Carbohydrates. JULIUS STOKLASA, JOHANN ŠEBOR, and WENZEL ZDOBNICKÝ (*Biochem. Zeitsch.*, 1913, **54**, 330—332. Compare this vol., i, 18).—A further reply to the criticisms of Walther Löb (this vol., i, 250).

Behaviour of Cellulose Towards Pure Nitric Acid. II. CARL HAEUSSERMANN (*Zeitsch. angew. Chem.*, 1913, **26**, 456. Compare *Zeitsch. angew. Chem.*, 1910, **23**, 1761).—"Sulphite cellulose" is converted by cold concentrated nitric acid into nitrates without undergoing marked structural change. Treatment with nitric acid, D 1·495, 1·48, 1·47, 1·46 and 1·40, leads to the formation of nitrates containing 11·1%, 9·6%, 8·0%, 7·5%, and 2·3% of nitrogen respectively. "Sulphite cellulose" dissolves readily in warm concentrated nitric acid, and the solution, when poured into cold water, yields an amorphous product, part of which is soluble in a mixture of alcohol and ether.

Hydrocellulose prepared from cotton when treated with nitric acid, D 1·5, 1·485, 1·48, and 1·40, yields hydrocellulose nitrates containing 13·0%, 9·5%, 8·9%, and 2·3% of nitrogen respectively, whilst hydrocellulose nitrates containing 11·2%, 8·8%, 6·6%, and 2·1% of nitrogen are obtained by the action of nitric acid, D 1·495, 1·48, 1·45 and 1·40 respectively, on hydrocellulose prepared from "sulphite cellulose."

The esters derived from "sulphite cellulose" closely resemble those derived from cotton in their behaviour towards solvents, but the higher cellulose and hydrocellulose nitrates prepared from "sulphite cellulose" are not completely soluble in acetone. W. H. G.

Benzoyl Esters of Cellulose. HERMANN OST and F. KLEIN (*Zeitsch. angew. Chem.*, 1913, **26**, 437—440. Compare Hauser and Muschner, this vol., i, 363; Briggs, this vol., i, 594).—An investigation on the benzoylation of cellulose, carried out primarily with the object of preparing a tribenzoate corresponding with the triacetate and trinitrate of cellulose.

Cellulose when treated with alkali hydroxide and benzoyl chloride yields a mixture of benzoates, the benzoic acid content of which is between 0 and 77%, and is dependent mainly on the proportions in which the reacting substances interact and to a slight degree on the physical state of the cellulose employed. A maximum yield of 218% of product is obtained by using a 22·4% sodium hydroxide solution in

the molecular proportions of 30 of sodium hydroxide to 1 of cellulose and 3 of benzoyl chloride to 4 of sodium hydroxide, whilst by using a 31·4% potassium hydroxide solution a maximum yield of 211% of product is obtained, the molecular proportions being the same as those just cited. The yields of product increase regularly with increase in the concentrations of the alkali up to the strengths quoted; at higher concentrations of the alkali the yields gradually decrease, and curves representing the relationship between alkali concentration and percentage of benzoic acid in the product do not show a "break" as do curves connecting alkali concentrations with the proportion of sodium combined with the cellulose (compare Vieweg, A., 1907, i, 893). A second and third treatment with alkali and benzoyl chloride increases the yield to 224% and 226% respectively, but it has not been found possible by the Schotten-Baumann method to pass beyond these values; the portion of the latter product soluble in chloroform contained 72·7% of benzoic acid, corresponding approximately with 2·5 benzoyl groups to the $C_6H_{10}O_5$ complex.

The crude benzoates may be fractionally separated by solvents; chloroform extracts 5 to 10% of a mixture containing 68 to 70% benzoic acid; aniline extracts from the portion insoluble in chloroform a mixture containing 61 to 65% of benzoic acid, whilst aniline-phenol (1:1) extracts from the residue a mixture containing 59 to 60% of benzoic acid.

Benzoates containing up to 77% of benzoic acid (a tribenzoate would contain 77·2%) are obtained by treating cellulose with benzoyl chloride in the presence of nitrobenzene and pyridine at 110—130°; the highest esters are formed when the quantity of pyridine employed is insufficient to keep the solution basic or neutral.

Solutions of cellulose benzoates in chloroform are dextrorotatory; the following values are given: tribenzoate, $[\alpha]_D$ 26—27°; ester with 70—72% of benzoic acid, $[\alpha]_D$ 20—22°.

Mercerised cellulose does not react more readily than finely divided cotton. Cellulose regenerated from "young" viscose is more reactive than that from "old" viscose; the benzoate from the former gave elastic films, whilst the benzoate from the latter gave films which were very brittle.

The yield of benzoate from hydrocellulose is less than that from cellulose, but 50% of the product containing 71—72·4% of benzoic acid is soluble in chloroform.   W. H. G.

Chemical Reactions Induced by Bacteria aceti. H. J. WATER-MAN (*Chem. Weekblad*, 1913, 10, 718—730).—*B. aceti* isolated at low temperature rapidly transform aldoses, such as dextrose and galactose, into the corresponding monobasic acids, but has no action on ketoses. *B. aceti* isolated at high temperature does not react with either aldoses or ketoses. A summary of previous work on the action of *B. aceti* is given.   A. J. W.

d-Ribose. W. ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1913, 10, 664).—d-Ribose has been synthesised by converting d-gluconic acid into d-arabinose by the action of hydrogen peroxide, transformation of the pentose into d-arabonic acid by means

of, bromine water, and conversion of this acid into *d*-ribonic acid by heating with pyridine. The ribonic acid was separated from arabonic acid by fractional crystallisation of the phenylhydrazides, and had m. p. 80° and $[a]_D$ +18·4°. On reduction with sodium amalgam, it yielded *d*-ribose, purified by conversion into its *p*-bromophenylhydrazone, m. p. 164°. The hydrazone was transformed into *d*-ribose by the action of benzaldehyde. It forms colourless, hygroscopic crystals, m. p. 95°, $[a]_D$ − 21·5°.　　　　　　　　　　　　　A. J. W.

The Oxidation of *d*-Glucose in Alkaline Solution by Air as Well as by Hydrogen Peroxide. J. W. E. GLATTFELD (*Amer. Chem. J.*, 1913, **50**, 135—157).—The author has repeated the oxidation of *a*-glucose by hydrogen peroxide and air in potassium hydroxide solution, and finds that in addition to glycollic acid, formic acid and carbon dioxide, isolated by Spoehr (A., 1910, i, 221) from the oxidation product, *d*-erythronic, *l*-threonic and *dl*-glyceric acids are produced.

Spoehr's *a*-hydroxymethyl-*d*-arabonic acid is found to be identical with *d*-arabonic acid.

The formation of the latter acid proves that glucose in the form of its *aβ*-dienol, $HO\cdot CH:C(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH$, dissociates into hydroxymethylene, $HO\cdot CH:$, and the methylenenol of *d*-arabinose, $:C(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH$, which is then oxidised to *d*-arabonic acid. Oxidation of the dissociation products of the *βγ*-dienol,

$$HO\cdot CH_2\cdot C(OH):C(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot OH,$$

gives rise to glycollic, *d*-erythronic and *l*-threonic acids, whilst the glyceric acid is formed by the dissociation and subsequent oxidation of the *γδ*-dienol, $HO\cdot CH_2\cdot CH(OH)\cdot C(OH):C(OH)\cdot CH(OH)\cdot CH_2\cdot OH$ (compare Nef, A., 1908, i, 5).

For details of the method employed in separating the oxidation products, the original must be consulted.

The following new salts are described : *cinchonine* d-*arabonate*, m. p. 170—180°, $[a]_D^{20}$ +120·3° in water, and the corresponding *strychnine* salt, decomp. 167—170°, $[a]_D^{20}$ −26·08°, *quinine* salt, m. p. 172—173°, $[a]_D^{20}$ − 106·2°, and *brucine* salt, m. p. 167—170°, $[a]_D^{20}$ − 26·33°.

The *strychnine* salt of *d*-erythronic acid has m. p. 198—199°, $[a]_D^{20}$ − 16·84° ; the *quinine* salt, m. p. 166°, $[a]_D^{20}$ − 106·9°.　　F. B.

Biochemical Synthesis of Galactosides of Alcohols. V. *β-iso*Butylgalactoside. ÉMILE BOURQUELOT and MARC BRIDEL (*J. pharm. chim.*, 1913, [vii], **8**, 108—109).—A mixture of 95 parts of *iso*butyl alcohol by weight and 5 parts of water was kept for four months with galactose and emulsin. *β-isoButylgalactoside* was obtained in colourless needles of bitter taste, $[a]_D$ − 11·23°.

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Phosphates of Magnesium and Amines. LÉONCE BARTHE (*Bull. Soc. chim.*, 1913, [iv], **13**, 821—824).—The only double phosphate of magnesium and amines that has been prepared is magnesium methylamine phosphate (Barthe, A., 1905, i, 546 ; François, A., 1908,

i, 505). Unsuccessful attempts to prepare the corresponding salt from ethylamine are now described.

When ethylamine is added to a solution of magnesium hydrogen phosphate in dilute phosphoric acid in quantity more than sufficient for saturation, a colloidal precipitate is formed which becomes crystalline after several hours and consists entirely of magnesium phosphate. The mother liquors, when concentrated, deposit ethylamine phosphate and a further quantity of magnesium phosphate. If an excess of ethylamine is avoided, a crystalline precipitate is obtained after some hours, analysis of which shows it to be a mixture of magnesium ethylamine phosphate and magnesium phosphate or of ethylamine phosphate and magnesium phosphate. When the phosphoric acid is replaced by hydrochloric or sulphuric acids, magnesium phosphate is similarly precipitated. Analogous results are obtained by the solution of magnesium hydrogen phosphate in ethylamine hydrochloride and subsequent addition of the free amine.

Magnesium hydrogen phosphate, $MgHPO_4,7H_2O$, is most readily obtained by mixing equal volumes of 2% magnesium sulphate solution and 3% disodium hydrogen phosphate solution. A gelatinous precipitate is immediately obtained, which is rapidly transformed into a mass of fine needles.   H. W.

Preparation of the Nitrites of the Primary, Secondary, and Tertiary Amines by the Interaction of the Hydrochlorides of the Bases and Alkali Nitrites. PANCHANAN NEOGI (*Chem. News*, 1913, 108, 53—55, 62—65).—A full account of work of which an abstract has already appeared (P., 1913, 29, 112).   W. G.

The Double Cadmium and Mercuric Iodides of Substituted Ammonium Bases. RASIK LAL DATTA (*J. Amer. Chem. Soc.*, 1913, 35, 949—955).—The following cadmium compounds were prepared either by adding cadmium chloride to an excess of the substituted ammonium iodide (compare T., 1913, 103, 426), or by mixing solutions of cadmium iodide and the ammonium iodide in the requisite proportions. Two types of salts are obtained, namely, $2NR_4I,CdI_2$ and NR_4I,CdI_2, of which the latter is produced only in exceptional cases. The salts are white powders, sparingly soluble in water.

The double salts of cadmium iodide with *tetramethylammonium, tetraethylammonium,* p-*tolyltrimethylammonium, pyridinium,* a-*picolinium,* and *quinolinium* iodides are of the type $2NH_4I,CdI_2$; *tetrapropylammonium iodide* gives the salt NPr_4I,CdI_2.

When an aqueous solution of mercuric chloride is added to an excess of alkylammonium iodide, a white to yellowish-white precipitate is formed, of the type $2NR_4I,HgI_2$. If the addition of mercuric chloride be continued, the precipitate changes to yellow and the salt is of the type $2NR_4I,3HgI_2$; further addition of mercuric chloride gives mercuric iodide. A solution of mercuric iodide in potassium iodide may be used instead of mercuric chloride; when the interacting solutions are strong, the type $2NR_4I,HgI_2$ is produced, but this is decomposed by water and changed to the type $2NR_4I,3HgI_2$, which is the most stable of all, and is prepared by the interaction of dilute

solutions, using an excess of potassium mercuric iodide solution. The following substituted ammonium iodides give salts of both types: *Tetramethylammonium, tetraethylammonium,* and *trimethylsulphonium* (compare Smiles, T., 1900, **77**, 160) *iodides.* The following iodides give salts of the type $2NR_4I,HgI_2$: *tetrapropylammonium,* p-*tolyl-trimethylammonium, pyridinium* and *quinolinium iodides.* p-*Tolyl-trimethylammonium iodide* also gives the salt, $C_6H_4Me \cdot NMe_3I,HgI_3$.

The above salts, for the most part, vary in colour from a pale to a bright lemon yellow. They are all decomposed quantitatively into mercuric iodide on boiling with dilute nitric acid. T. S. P.

Platini-iodides of Substituted Ammonium and Sulphonium Bases. RASIK LAL DATTA (*J. Amer. Chem. Soc.,* 1913, **35**, 1185—1188).—It is found that although the platini-iodides of sodium and of the alkaline-earth metals cannot be obtained as precipitates by the interaction of chloroplatinic acid with concentrated solutions of the iodides (Datta, T., 1913, **103**, 426), this method proves very convenient for the preparation of the platini-iodides of potassium, ammonium, and the amines. The method failed with hydrazine hydriodide on account of the reduction of the chloroplatinic acid to metallic platinum. In other cases the condition necessary to success is the employment of an excess of the iodide of the metal or base.

The following substances were prepared : potassium platini-iodide, very soluble, black, crystalline powder ; ammonium platini-iodide, black powder ; *dipropylammonium platini-iodide,* black ; *tetrapropylammonium platini-iodide,* chocolate coloured ; a-*picolinium platini-iodide,* black ; *quinolinium platini-iodide,* jet black ; *trimethylsulphonium platini-iodide,* black powder ; *triethylsulphonium platini-iodide,* chocolate coloured.

D. F. T.

Non-equivalence of the Five Valencies of Nitrogen. EMIL FROMM (*Annalen,* 1913, **399**, 366—370).—By reason of the great importance of the subject, Meisenheimer's recent proof (this vol., i, 595) of the non-equivalence of the five valencies of the nitrogen atom must be submitted to searching criticism before being accepted. The author is of opinion that Meisenheimer's experiments can be interpreted in another, and more probable, manner. Meisenheimer assumes that hydrogen chloride and methyl iodide both attack trimethylamine oxide at the same point and in the same manner, yielding the additive compounds $NMe_3{<}^{OH}_{Cl}$ and $NMe_3{<}^{OMe}_{I}$ respectively. From the former by the action of sodium methoxide, and from the latter by moist silver oxide, are obtained the substances $NMe_3{<}^{OH}_{OMe}$ and $NMe_3{<}^{OMe}_{OH}$; the different behaviour of the two substances during decomposition is the foundation of Meisenheimer's proof of the difference of the fifth "unique" valency of nitrogen from the other four. The author takes exception to this. The two substances $NMe_3{<}^{OH}_{OMe}$

and $NMe_3{<}^{OMe}_{OH}$, being alcoholates of a very feeble base, $NMe_3(OH)_2$, must both be hydrolytically dissociated by water, and yield MeOH and $NMe_3(OH)_2$ if they have the constitutions given above. He is of opinion that hydrogen chloride and methyl iodide do not attack trimethylamine oxide in the same manner. With methyl iodide the oxide forms the methiodide, $NMe_3{:}O{<}^{Me}_{I}$; the product of the action of moist silver oxide is then $NMe_3{:}O{<}^{Me}_{OH}$, which would be expected to yield trimethylamine, formaldehyde, and water by its decomposition, as is actually the case.

The formula $NMe_3{:}O{<}^{Me}_{I}$ has been discussed and rejected by Meisenheimer (*loc. cit.*); the author, however, shows that the reasons for its rejection are insufficient.   C. S.

Non-equivalence of the Five Valencies of Nitrogen. JAKOB MEISENHEIMER (*Annalen*, 1913, **399**, 371—376).—The author replies to Fromm's criticisms (preceding abstract). In answer to his contention that two isomeric compounds should be produced by the addition of hydrogen chloride at the double linking of trimethylamine oxide if the fourth and the fifth valencies of the nitrogen atom are fundamentally different, the author claims that the whole behaviour of ammonium compounds proves that four of the valencies of the nitrogen atom are negative and the fifth is positive ; therefore, in the addition of hydrogen chloride to trimethylamine oxide, the negative chlorine will become attached only to the fifth positive valency of the nitrogen atom, and only one additive compound will be produced.

To Fromm's criticism that the two isomerides, $NMe_3{<}^{OH}_{OMe}$ and $NMe_3{<}^{OMe}_{OH}$, should both be hydrolysed by water, the author replies that only one, namely, that in which the methoxy-group is attached to the fifth positive valency of the nitrogen atom, should be hydrolytically dissociated ; the other isomeride, in which the methoxy-group is bound by a negative valency, should be as little affected by water as is methoxylamine, $OMe{\cdot}NH_2$.

The author also criticises adversely Fromm's reasons for ascribing oxonium formulæ to substances of the types $NMe_3Cl{\cdot}OMe$ and
$$NMe_3(OEt){\cdot}OMe.$$ C. S.

[**Non-equivalence of the Five Valencies of Nitrogen.**] EMIL FROMM (*Annalen*, 1913, **399**, 377).—The author agrees with Meisenheimer (preceding abstract) that in ammonium compounds the fifth "positive" valency of the nitrogen atom is different from the other four "negative" valencies, but is of opinion that the results of observations on ammonium compounds cannot be applied to the case of the amino-oxides without further consideration. He claims that in amino-oxides there are two "positive" valencies which differ from the other three "negative" valencies.   C. S.

Decomposition of Glucosamine by Bacteria. EMIL ABDER-
HALDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1913, 87,
214—219).—Glucosamine hydrochloride, when decomposed by micro-
organisms of the *B. subtilis* group, yields propionic acid and *d*-lactic
acid.   E. F. A.

Fermentative Decomposition of Creatinine. DANKWART
ACKERMANN (*Zeitsch. Biol.*, 1913, 62, 208—216).—Creatinine, mixed
with a little dextrose and peptone, was inoculated with bacteria from
a decomposing pancreas. Neither methyl- nor dimethyl-guanidine
was formed, the main product of the change being l-methylhydantoin,
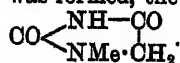
$$CO\underset{NMe\cdot CH_2}{\overset{NH-CO}{\big<}}.$$
                                                                     E. F. A.

The Changes Produced in Asparagine by Heating its
Aqueous Solutions. FELIX EHRLICH and FRITZ LANGE (*Biochem.
Zeitsch.*, 1913, 54, 256—276).—By heating the ordinary asparagine
with water for twelve hours and allowing the substance to crystallise
out in fractions, a very small amount was obtained which has
$[\alpha]_D^{20}\ 46\cdot2°$; this apparently *d*-asparagine (compare Erlenmeyer, this
vol., i, 836). The authors also show that when asparagine solutions
are heated, ammonia is evolved, and on crystallisation, crystals
together with a non-crystallising syrup are obtained. The longer the
heating takes, the smaller is the amount of crystals, the larger
the amount of syrup obtainable, and the larger is the quantity of
ammonia evolved. The uncrystallisable syrup is not readily freed
from ammonia, and the evidence obtained indicates that it contains
ammonium aspartate. The latter substance readily crystallises from
water, but if its solution is heated, an uncrystallisable syrup is also
obtained. It appears, therefore, to be an intermediate product
produced by the action of heat on asparagine solutions. The actual
nature of the final products has not yet been ascertained. S. B. S.

Resolution of *dl*-Aminohexoic Acid (Norleucine) into the
Optically Active Components by means of the Formyl
Compound. Polypeptides Derived from α-Aminohexoic Acid.
EMIL ABDERHALDEN, C. FROEHLICH, and DIONYS FUCHS (*Zeitsch. physiol.
Chem.*, 1913, 86, 454—468).—*dl*-α-Aminohexoic acid, which E. Fischer
resolved by means of the brucine salt, is readily resolved when the
brucine salts of the formyl derivatives are crystallised. The acid, for
which the name norleucine is proposed, has been combined with
glycine and leucylglycine to form polypeptides in the usual manner.

Formyl-dl-α-*aminohexoic acid* crystallises in lustrous needles, which
soften at 110—111°, m. p. 114°. The optical antipodes resemble each
other very closely, crystallising in slender, lustrous, short or long
needles aggregated in bunches. They soften at 111°, m. p. 114°, and
have $[\alpha]_D^{20}\ -15\cdot85°$ and $+15\cdot53°$ respectively.

Chloroacetyl-d-*norleucine* crystallises in colourless, transparent
lamellæ, which soften at 70°, m. p. 104—106°, $[\alpha]_D^{20}\ +3\cdot56°$.

Glycyl-d-*norleucine*, $CH_2\cdot[CH_2]_3\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CH_2\cdot NH_2$, forms

prisms growing into long needles, which become brown at 220°, sinter at 230°, m. p. 239—240°; they have $[a]_D^{20} - 8·71°$.

Glycyl-l-norleucine is almost identical in crystalline form and behaviour on heating ; it has $[a]_D^{20} + 8·24°$.

Chloroacetyl-dl-*norleucine* forms long prisms, m. p. 104—107°.

Glycyl-dl-*norleucine* separates in fatty plates or bundles of prisms ; it sinters at 210°, decomp. 215°.

a-Bromoisohexoylglycyl-dl-*norleucine* crystallises in platelets, m. p. 140°.

dl-*Leucylglycyl*-dl-*norleucine* separates as a crystalline skin. It sinters at 220°, decomp. 250°. It could not be hydrolysed by means of yeast juice with any certainty. The same applies to glycyl-*dl*-norleucine.   E. F. A.

Preparation of Derivatives of α-Bromoisovaleric Acid. ARTHUR LIEBRECHT (D.R.-P. 261877).—*a-Bromoisovalerylmethylamide*, needles, m. p. 103°, is obtained when α-bromoisovaleryl bromide is slowly dropped into a cooled 20% aqueous solution of methylamine (2 mols.) ; the corresponding *ethylamide*, needles, m. p. 120°, is prepared in a similar manner with ethylamine.   F. M. G. M.

Action of Hydrazine Hydrate on Dicyanodiamide and Biuret. ROBERT STOLLÉ and K. KRAUCH (*J. pr. Chem.*, 1913, [ii], 88, 306—314).—The authors have investigated the action of hydrazine hydrate on dicyanodiamide under various conditions, and find that in addition to guanazole, obtained by Hofmann and Ehrhart (A., 1912, i, 919), the following substances may be formed : aminodicyanodiamidine, 1-amino-2 : 5-dehydrazino-1 : 3 : 4-triazole, carbohydrazide, aminodiguanide, mono-, di- and tri-aminoguanidine.

With the exception of guanazole and the triazole, all the above-mentioned substances were isolated in the form of their benzylidene derivatives by acidifying the product of the reaction with hydrochloric acid and shaking with benzaldehyde.

The action of hydrazine hydrate on dicyanodiamide, both at 40° and at the ordinary temperature, results in the formation of guanazole, diaminoguanidine and triaminoguanidine ; if the reaction is carried out at 50°, these compounds are accompanied by aminoguanidine and *aminodiguanide*, which forms a *benzylidene* derivative, m. p. 287°, NH:C(NH$_2$)·NH(NH)·NH·N:CHPh.

Guanazole is best prepared by heating a mixture of dicyanodiamide (1 mol.) and hydrazine hydrate (2½ mol.) at 60—70° ; if the temperature is raised to 100—110°, carbohydrazide is formed simultaneously.

Nitrosoguanazole, $C_2H_4ON_6$, obtained as canary-yellow precipitate by the addition of sodium nitrite to a solution of guanazole in dilute acetic acid, is insoluble in the ordinary solvents, and on reduction with zinc dust and sulphuric acid yields guanazole and probably guanazine. When a large excess of hydrazine hydrate (5 mols.) is employed and the reaction carried out at 40°, dicyanodiamide yields guanazole and aminodicyanodiamidine (Thiele and Uhrfelder, A., 1899, i, 119) ; at the ordinary temperature, guanazole, mono-, di- and tri-aminoguanidine are formed, whilst at 70° 1-amino-2 : 5-hydrazino-1 : 3 : 4-triazole

(Stollé and Bowles, A., 1908, i, 474) is the main product. Excess of hydrazine hydrate at 100—110° leads to the formation of carbohydrazide.

When heated with hydrazine hydrate (4 mols.) at 108—118°, biuret yields the *hydrazine* salt of hydrazidicarboxylimide [2 : 5-diketotetrahydro-1 : 3 : 4-triazole], $\underset{\text{NH·CO}}{\overset{\text{NH·CO}}{\gtrdot}}$ NH,N₂H₄, which crystallises in needles, m. p. 195°, and is converted by shaking with benzaldehyde and dilute hydrochloric acid into benzalazine and hydrazidicarboxylimide (compare Pellizzari, A., 1895, i, 73) ; if the reaction is carried out at 80—85°, the hydrazine salt is accompanied by aminobiuret, which was isolated in the form of its benzylidene derivative, m. p. 207° (compare Thiele and Uhrfelder, A., 1899, i, 118).   F. B.

Some Hydrazine Derivatives of Chloral and Trichloroacetic Acid. ROBERT STOLLÉ and FR. HELWERTH (*J. pr. Chem.*, 1913, [ii], 88, 315—318).—Chloralhydrazine (Knöpfer, A., 1911, i, 704 ; this vol., i, 703) is readily obtained by the gradual addition of hydrazine hydrate to a well cooled ethereal solution of chloral hydrate. It separates from alcohol in white needles, m. p. 100° (Knöpfer gives 85°), and decomposes when kept, yielding hydrazine hydrochloride. With benzaldehyde in aqueous solution it forms the *benzylidene* derivative, CCl₃·CH(OH)·NH·N:CHPh, crystallising in small needles, m. p. 65° (decomp.).

s-Bistrichloroacetylhydrazide, m. p. 195°, N₂H₂(CO·CCl₃)₂, prepared by heating hydrazine monohydrochloride with trichloroacetyl chloride on the water-bath (compare L. and P. Spiegel, A., 1907, i, 507), reacts with alcoholic silver nitrate and ammonia, yielding a yellow *silver* derivative, and when heated with phosphorus pentachloride or thionyl chloride is converted into 2 : 5-*bistrichloromethyl*-1 : 3 : 4-*oxadiazole*, $CCl_3 \cdot C \underset{O}{\overset{N:N}{\gtrdot}} C \cdot CCl_3$, which has m. p. 121°/9 mm., and separates from ether in long prisms, m. p. 48°.   F. B.

*iso*Butyl Ester of Phosphorous Acid. I. ALEXANDER E. ARBUZOV and A. A. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 681—690).—*Diisobutylphosphorous acid*, P(O·C₄H₉)₂OH, obtained by Arbuzov's method for obtaining esters of this type (A., 1907, i, 8, 174, 275), is a colourless, mobile liquid with a pleasant, fruity odour, b. p. 117·5°/14 mm., 235—236°/760 mm., D_0^0 0·9941, D_{20}^{20} 0·9776, D_4^0 0·9940, D_4^{20} 0·9759. With metallic sodium it yields a sodium salt stable at high temperatures ; the *silver* salt, P(OC₄H₉)₂OAg, was analysed.

iso*Butyl phosphite*, P(O·C₄H₉)₃, separated from its mixture with the preceding compound (A., 1907, i, 8) by converting the latter into sodium salt and distilling, is a colourless, mobile liquid with an intense peculiar odour, b. p. 100·5°/4·5 mm., 234—235°/760 mm., D_0^0 0·9193, D_{20}^{20} 0·9052, D_4^0 0·9193, D_4^{20} 0·9036. It reacts with bromine according to the equations :

$$P(O \cdot C_4H_9)_3 + Br_2 = PBr_2(O \cdot C_4H_9)_3 = 2C_4H_9Br + PO_2 \cdot O \cdot C_4H_9.$$
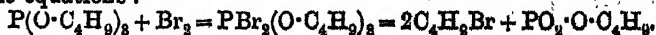
With cuprous iodide it forms the *compound*, $CuI,P(O \cdot C_4H_9)_8$, m. p. about 48°.

It is evident that the impossibility of separating the two esters, $P(O \cdot C_4H_9)_2 \cdot OH$ and $P(O \cdot C_4H_9)_8$, by fractional distillation is due to the fact that the two liquids and mixtures of them have almost identical boiling points.   T. H. P.

Isomeric Change of $P(OC_4H_9)_8$ **into** $C_4H_9 \cdot PO(OC_4H_9)_2$. II. ALEXANDER E. ARBUZOV and A. A. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 690—694).—When heated with *iso*butyl iodide, *iso*butyl phosphite (see preceding abstract) undergoes isomeric change in accordance with the equations :

$$C_4H_9I + P(O \cdot C_4H_9)_8 = I \cdot P(C_4H_9)(O \cdot C_4H_9)_3 =$$
$$PO(C_4H_9)(OC_4H_9)_2 + C_4H_9I.$$
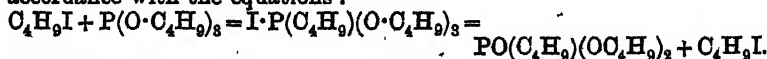
The *isobutyl isobutylphosphite* thus obtained is a colourless, mobile liquid, b. p. 133·5—134°/10 mm., 258—259°/760 mm., D_0^0 0·9630, D_{20}^{20} 0·9475, D_4^0 0·9628, D_4^{20} 0·9459. The corresponding *iso*butylphosphorous acid was obtained in crystals, $2O \vdots P(C_4H_9)(OH)_2,H_2O$, m. p. 124°; this acid was originally prepared by Hofmann (A., 1873, 883) as a waxy and evidently impure mass, m. p. 100°.   T. H. P.

Compounds of Boric Acid and Mannitol. FERNANDO AGENO and ELENA VALLA (*Gazzetta*, 1913, **43**, ii, 163—174).—Solubility measurements indicate that the combination of boric acid and mannitol takes place in equimolecular proportions. The stability constant at 25° is 0·598; it decreases when the temperature increases. The concentration of the hydrogen ions in solutions of mannitoboric acid has been determined, the dissociation constant being of the same order of magnitude as those of the monobasic organic acids, and it is proportional to the concentration of the mannitol. The rotatory power of solutions of sodium metaborate and mannitol is proportional to the concentration of the mannitol.   R. V. S.

Preparation of Readily Soluble Stable Compounds of Perborates. VEREINIGTE FABRIKEN FÜR LABORATORIUMSBEDARF (D.R.-P. 261633).—The following complex salts are prepared by mixing the required proportions of the components in aqueous solution and evaporating to dryness: *sodium borotartrates*, $C_4H_4O_6(BONa)$ or $C_4H_3NaO_6(BONa)$; *sodium borocitrates*, $(C_6H_5O_7)_2(BONa)_3$ or
$$(C_6H_4NaO_7)_2(BONa)_3;$$
aluminium sodium tartrates, $NaOAl(C_4H_4O_6)_2Na_2$ or $Al(C_4H_4O_6)_2Na_3$ When moist they are of a syrupy consistency, but can be dried to masses resembling water glass and then reduced to powder.
                                  F. M. G. M.

Preparation of Chlorobenzenedisulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 260563).—When *p*-chlorobenzenesulphonyl chloride is heated with fuming sulphuric acid (4 parts) at 160—180° with continual stirring, it furnishes a chlorobenzenedisulphonic acid (compare A., 1892, 331).   F. M. G. M.

Preparation of *meso*Halogenanthracene-β-sulphonic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 260562).—*Dichloroanthracenesulphonic acid*, a yellow powder, somewhat soluble in and exhibiting a blue fluorescence in water, is obtained when dichloroanthracene (1 part) in chloroform (100 parts) at 30° is treated with chlorosulphonic acid and the temperature subsequently maintained at 40° for four hours; the reaction can also be carried out in fuming sulphuric acid.

Dibromoanthracenesulphonic acid is obtained in a similar manner from dibromoanthracene. F. M. G. M.

Preparation of Iodo-derivatives of *p*-Hydroxy-β-phenylethylamine and of its *N*-Alkyl Derivatives. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 259193).—The iodo-derivatives of *p*-hydroxy-β-phenylethylamine have an enhanced therapeutic value. *Di-iodo-p-hydroxy-β-phenylethylamine*, glistening, colourless needles, m. p. 189—190°, is obtained when an aqueous solution of *p*-hydroxy-β-phenylethylamine is slowly treated with iodine and sodium hydroxide; any great excess of alkali is to be avoided during the reaction; the *hydriodide* separates in yellowish-brown leaflets, and is decomposed with sodium carbonate in the usual manner.

N-Benzyl-p-hydroxy-β-phenylethylamine hydrochloride,

$$OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NH \cdot CH_2Ph, HCl,$$
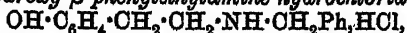
needles, m. p. 216°, is prepared from benzaldehyde and *p*-hydroxy-β-phenylethylamine with subsequent reduction (with sodium amalgam) of the Schiff *base*, $OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot N:CHPh$; when treated with iodine, it furnishes N-*benzyldi-iodo*-p-*hydroxy-β-phenylethylamine*, yellow needles, m. p. 159—160° (decomp.).

Piperonyl p-*hydroxyphenylethylamine*, m. p. 115° (the *hydrochloride* has m. p. 219°), on similar treatment gives rise to a N-*piperonyldi-iodo*-p-*hydroxyphenylethylamine*, decomp. m. p. 165°. F. M. G. M.

Preparation of *N*-Alkylaryl Derivatives of *p*-Hydroxy-β-phenylethylamines. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 259874). —The Schiff base obtained from benzaldehyde and *p*-hydroxy-β-phenylethylamine (compare preceding abstract) has m. p. 148°; N-*benzyl*-p-*hydroxy-β-phenylethylamine* forms colourless needles, m. p. 143°; whilst the Schiff *base* (*loc. cit.*) prepared from piperonaldehyde and *p*-hydroxy-β-phenylethylamine has m. p. 151°.

When *p*-hydroxy-β-phenylethylamine is combined with veratraldehyde it furnishes a Schiff *base*, m. p. 114°, which on reduction gives rise to N-*veratryl*-p-*hydroxy-β-phenylethylamine*, m. p. 118°; the *hydrochloride* has m. p. 215°, whilst with salicylaldehyde it yields a Schiff *base*, yellow needles, m. p. 145°, and on reduction N-*o-hydroxybenzyl*-p-*hydroxy-β-phenylethylamine*, colourless needles, m. p. 115°.

F. M. G. M.

The Condensation of Vanillin and Piperonal with Certain Aromatic Amines. ALVIN S. WHEELER (*J. Amer. Chem. Soc.*, 1913, **35**, 976—978. Compare A., 1909, i, 673; 1908, i, 332; 1903, i, 246). —An extension of the earlier investigations. In boiling toluene

solution, vanillin slowly condenses with p-aminobenzoic acid with formation of *4-hydroxy-3-methoxybenzylidene-p-aminobenzoic acid*, deep yellow plates, m. p. 211—212°, which on recrystallisation from water separates as a brilliant red substance with one molecule of water ; on expelling the water at 100° the original yellow colour is restored.

Vanillin condenses with ethyl p-aminobenzoate in boiling benzene solution, giving *ethyl 3-methoxy-4-hydroxybenzylidene-p-aminobenzoate*, thin, yellow plates, m. p. 145° (corr.).

Under similar conditions to the last, vanillin and p-anisidine produce *4-hydroxy-3-methoxybenzylidene-p-anisidine*, pale yellow crystals forming radiating clusters, m. p. 133·5° (corr.) ; with piperonal and p-anisidine, *3 : 4-methylenedioxybenzylidene-p-anisidine*, very pale yellow needles, m. p. 117·5° (corr.), is obtained.

Piperonal and p-aminobenzoic acid condense slowly in boiling toluene solution, yielding *3 : 4-methylenedioxybenzylidene-p-aminobenzoic acid*, pale yellow prisms, 233—234°. If the heating is less prolonged, or if an excess of the acid is taken, a *substance*, m. p. 171—173°, is obtained in considerable quantity.

When heated together in boiling benzene solution, piperonal and ethyl p-aminobenzoate undergo condensation to *ethyl 3 : 4-methylenedioxybenzylidene-p-aminobenzoate*, long, pale yellow needles, m. p. 109° (corr.).   D. F. T.

Preparation of Benzoylchloroamide. RASIK LAL DATTA and TARAPADA GHOSH (*J. Amer. Chem. Soc.*, 1913, **35**, 1044—1045).— Benzoylchloroamide is conveniently prepared by passing chlorine into an aqueous suspension of powdered benzamide until a sample of the solid, after separation and recrystallisation, has m. p. 116° ; the process usually occupies several hours.

If the method used by Bender (*Ber.*, 1882, **15**, 410) for the preparation of this substance is modified by adding acetic acid and then a concentrated solution of bleaching powder to an aqueous suspension of benzamide, the product is a *substance*, m. p. 153—163°.
                                                                           D. F. T.

Molecular Rearrangements of Carbon Compounds. II. Aromatic (N)-Acylamines and the Beckmann Rearrangement. CLARENCE G. DERICK and J. H. BORNMANN (*J. Amer. Chem. Soc.*, 1913, **35**, 1269—1289. Compare Derick, A., 1910, i, 805).—Further experimental evidence is produced in favour of the decision in the earlier investigation that non-reversible intramolecular rearrangements of carbon compounds take place in the direction to decrease the ionisation constant. For the purpose of determination of the small ionisation constants of acylamines, a colorimetric method based on the colours produced with suitable indicators has been developed, by means of which the ionisation constant of sufficiently soluble acids and bases may be estimated with a mean error of 2%.

In accord with the view expressed above it is found that each of such substances as acetanilide, propionanilide, benzanilide, and chloroacetanilide, which do not rearrange to monoacylaminoketones, has a

lower ionisation constant (basic) than the corresponding isomeride of the latter type. On the other hand, the aromatic diacylamides, for example, diacetanilide and dipropionanilide, which can undergo rearrangement (Chattaway, T., 1904, 386, 1181, etc.), are found to have higher ionisation constants (acidic) than their isomerides, p-acetylaminoacetophenone and p-propionylaminopropiophenone, which ionise as bases.

The results generally indicate that acyl radicles derived from acids with ionisation constants between 1.4×10^{-5} and 1.55×10^{-3} at 25° must be twice substituted at the nitrogen atom of aniline before isomeric change will be possible.

In the case of the Beckmann rearrangement, which has been studied with acetophenoneoxime and benzophenoneoxime, it is again found that the ionisation constants (basic) of these substances are greater than those of acetanilide and benzanilide, into which they pass by isomeric change.

p-*Propionylaminopropiophenone*, long, colourless needles, m. p. 151° (corr.), was obtained by the action of propionyl chloride on p-aminopropiophenone, and also by warming propionylanilide with propionyl chloride and aluminium chloride in carbon disulphide. The method adopted by Čech (A., 1878, 51) proved unsatisfactory for the preparation of chloroacetanilide, and it was found that much better results were obtainable by allowing aniline and chloroacetic acid to react in cooled ethereal solution and keeping the resulting aniline chloroacetate with the calculated quantity of phosphoric oxide in a well stoppered bottle for several weeks. D. F. T.

A New Method of Synthesising the Higher Phenols. TREAT B. JOHNSON and WILLARD W. HODGE (*J. Amer. Chem. Soc.*, 1913, 35, 1014—1023).—It is found that mixed ketones containing hydroxyl or alkyloxyl radicles in the benzene nucleus are readily and smoothly reducible by zinc amalgam and hydrochloric acid to form the corresponding alkyl-substituted phenols or ethers. The reaction appears to be a general one. Only those products which are described for the first time are mentioned below.

1-Acetyl-2 : 4-dihydroxybenzene is reduced by the above agent to 2 : 4-*dihydroxy-1-ethylbenzene*, prismatic crystals, m. p. 98—99°. The corresponding propionyl compound gives 2 : 4-*dihydroxy-1-propylbenzene* prisms, m. p. 82—83°.

2-Propionyl-1 : 4-dihydroxybenzene becomes converted into 1 : 4-*dihydroxy-2-propylbenzene*, microscopic needles, m. p. 86°. 2-*Propionyl-1 : 4-dimethoxybenzene*, a pale yellow oil, b. p. 167—169°/13 mm., obtained by the action of propionyl chloride and aluminium chloride on a solution of quinol dimethyl ether in light petroleum, on reduction yields 1 : 4-dimethoxy-2-propylbenzene (Thoms, A., 1903, i, 415).

It is noteworthy that whereas the reduction of 1-chloroacetyl-3 : 4-dihydroxybenzene by this new method proceeds satisfactorily giving a good yield of 3 : 4-dihydroxy-1-ethylbenzene, the action of zinc and hydrochloric acid, as has already been shown (Dziergowski, A., 1894, i, 73), leads only to the formation of 1-acetyl-3 : 4-dihydroxybenzene. D. F. T.

Triphenylmethyl. XXIII. Tautomerism of the Hydroxy-triphenylcarbinols. MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1913, **35**, 1035—1042).—The conflicting results as to the properties of *p*-hydroxy-triphenylcarbinol (Bistrzycki and Herbst, A., 1903, i, 639; 1904, i, 44; Baeyer and Villiger, A., 1903, i, 813; Auwers and Schröter, A., 1903, i, 820) are readily explicable when it is borne in mind that tautomerism has been observed with such related compounds as triphenylmethyl and the triarylcarbinyl haloids (A., 1909, i, 144). There exist two forms of hydroxytriphenylcarbinol, probably of the benzenoid structure, $OH \cdot CPh_2 \cdot C_6H_4 \cdot OH$, and the quinonoid structure, $CPh_2 : C_6H_4 \diagdown_{OH}^{H}$, respectively.

The hydroxycarbinol is best prepared by demethylating *p*-anisyl-diphenylcarbinol with aluminium chloride in benzene. The product is digested with 3% sodium hydroxide solution, when, after filtration, the addition of excess of acetic acid precipitates the yellow quinonoid modification; this, after recrystallisation from 40—50% acetic acid, has m. p. 139—140°, whilst separation of the carbinol from the alkaline solution by addition of ammonium chloride solution gives the colourless benzenoid form, which, after crystallisation from aqueous alcohol containing a little ammonia, forms needles or plates, m. p. 157—159°, or sometimes 162—163° (compare Auwers and Schröter, *loc. cit.*).

The two forms are not physical isomerides, for a solution of each crystallises only in the original form even when inoculated with a crystal of the other. On heating the solids, the quinonoid modification commences to undergo dehydration below 60°, whilst the benzenoid modification begins to turn yellow in the neighbourhood of 100°, probably due to isomerisation, and simultaneously commences to lose water.

The yellow modification is always obtained when either form is crystallised from acetic acid, whilst the colourless modification is invariably the result if an alkaline solution is treated with ammonium chloride or if crystallisation is effected from alcohol containing some ammonia. Recrystallisation of either form from alcohol containing hydrochloric acid usually gives a mixture of yellow and colourless crystals, whilst alcohol alone induces tautomerisation but slowly.

Exposure to sunlight or ultraviolet radiation causes a fairly rapid and complete change of the colourless benzenoid to the yellow quinonoid tautomeride, so that, from analogy to the stereoisomeric ethylenic compounds, the latter is presumably the labile modification.

Hydrogen chloride is absorbed by both isomerides in the solid state with formation of the same chloride, $CPh_2 : C_6H_4 \diagdown_{OH}^{Cl}$, a deep red, iridescent solid apparently identical with the product of the action of hydrogen chloride on fuchsone; when treated with molecular silver this *p*-hydroxytriphenylcarbinyl chloride loses hydrogen chloride and gives rise to fuchsone.

It is found that this behaviour is apparently general for the *p*-hydroxytriphenylcarbinols, and that, also, *o*-cresyldiphenylcarbinol (compare Bistrzycki and Zurbriggen, A., 1904, i, 44) gives two modifications which can be best isolated by the methods applied above;

there exists similar relations between the modifications of high and low m. p., as regards colour and behaviour towards light. D. F. T.

Identification of "Jambulol" as Ellagic Acid. FREDERICK B. POWER and THOMAS CALLAN (*Pharm. J.*, 1913, **91**, 245).—Further examination of the substance present in jambul seeds, to which the name "jambulol" was given previously by the authors (A., 1912, ii, 480) shows that it is identical with ellagic acid (compare T., 1905, 87, 1412). W. P. S.

The Crystalline Deposit Occurring in the Timber of the "Colonial Beech" [Gmelina Leichhardtii, F.v.M.]. HENRY G. SMITH (*J. Roy. Sci. New South Wales*, 1913, **46**, 187—200).—The author has examined the white deposit which frequently fills the cells of the wood and accumulates in the cracks of *Gmelina Leichhardtii*; he proposes to name this, *gmelinol*. It separates from hot water in needle prisms or plates. In the crystalline state it has m. p. 122° (corr.) and, after cooling, solidifies to a transparent, resin-like substance, m. p. 62—63°. The latter m. p. remains unchanged after many weeks if the material is preserved in the glassy condition in the lump, but, if the fused substance is powdered, the m. p. immediately commences to rise, and, after a comparatively short time, has reached about 120—121°, but does not appear to revert quite to the m. p. of the original crystals. It has $[a]_D$ +123·3° when dissolved in chloroform. It dissolves in 1470 parts of water at 22°. Analyses and determination of molecular weight indicate the formula $C_{19}H_{14}O_4$. Nitric acid converts it into a *dinitro*-compound, $C_{19}H_{12}O_4(NO_2)_2$, m. p. 128—129°. Sodium acetate and acetic anhydride transform it into a *monoacetyl* derivative, m. p. 110°.

When an excess of bromine water is added to an aqueous solution of the substance, a light drab *substance*, $C_{12}H_{13}O_4Br$, is formed, which is not distinctly crystalline, and melts at about 100°, after much darkening at about 90°. The bromine atom must have been introduced into the side-chain, since it can be eliminated by boiling with alcoholic silver nitrate solution. Zeisel determinations indicate the presence of two methoxy-groups, and this is confirmed by the production of veratric acid when the substance is oxidised by a
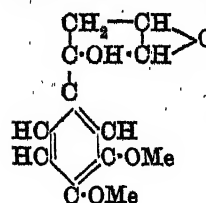
solution of chromic acid in glacial acetic acid, or by alkaline permanganate. When fused with potassium hydroxide at a temperature not exceeding 200°, phenolic substances are formed, whilst, at 210—225°, protocatechuic acid is produced, together with small quantities of a volatile acid.

From the above experiments, and from the red and green colorations given by the vapour of the substance to pine wood moistened with hydrochloric acid, the author is led to propose tentatively the annexed formula for gmelinol. H. W.

Preparation of *N*-Monoalkyl Derivatives of *p*-Aminophenols. EMMANUEL MERCK (D.R.-P. 260234. Compare A., 1909, i, 222).— *N*-Alkyl derivatives of *p*-aminophenols are readily prepared by the

action of primary aliphatic amines on the alkali derivatives of quinol at a temperature of 200—250° for five to twenty hours, either in the presence or absence of condensing agents ; this reaction, moreover, can be carried out in aqueous solution or in the absence of a solvent.

Details are given of several modifications of these methods for preparing N-methyl-p-aminophenol from methylamine and quinol in the presence of sodium ethoxide, or of sodium carbonate either with or without the addition of zinc chloride or other condensing agents.   F. M. G. M.

Derivatives of Phenacyl Sulphide and their Stereoisomerism. EMIL FROMM and WILHELM SCHÖMER (*Annalen*, 1913, 399, 353—365).—*Dibenzylidenediphenacyl sulphide*, $S(CBz:CHPh)_2$, m. p. 270°, leaflets, is obtained from phenacyl sulphide, benzaldehyde, and sodium hydroxide in 50% alcohol. Diphenacyl sulphide and bromine in chloroform at 0° yield at first a yellow precipitate of the unstable *diphenacyl sulphide dibromide*, but ultimately *dibromodiphenacyl sulphide*, $C_{16}H_{12}O_2SBr_2$, m. p. 107°, white crystals, is obtained. The *di-iodide*, $I_2S(CH_2 \cdot COPh)_2$, m. p. 121°, red needles, is more stable, and is prepared in a similar manner.

Equal molecular quantities of diphenacylsulphoxide and phenylhydrazine in neutral or in acid solution yield *diphenacylsulphoxidephenylhydrazone*, $C_{22}H_{20}O_2N_2S$, m. p. 186°. Diphenacylsulphoxide and hydroxylamine hydrochloride, with or without sodium carbonate, yield *diphenacylsulphoxidedioxime*, $C_{16}H_{16}O_3N_2S$, m. p. 206°; no other oxime or dioxime has been obtained.

Dimethyldiphenacylsulphone has the symmetrical formula,
$$SO_2(CHMe \cdot COPh)_2,$$
since it is decomposed by boiling dilute sodium hydroxide into benzoic acid and diethylsulphone. Unlike diphenacylsulphone itself, dimethyldiphenacylsulphone does not condense with phenylhydrazine, semicarbazide, or hydroxylamine in acid, neutral, or alkaline solution. This inactivity apparently must be due to steric hindrance ; it is not to be attributed to the existence of the sulphone in the form $SO_2(CMe:CPh \cdot OH)_2$, because the substance does not react with acetic anhydride, benzoyl chloride, or sodium and chlorodinitrobenzene.
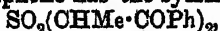
Diphenacylsulphone and aqueous bromine in daylight yield *dibromodiphenacylsulphone*, $C_{16}H_{12}O_4Br_2S$, m. p. 186°, prisms, after eight days, and *tetrabromodimethylsulphone*, $SO_2(CHBr_2)_2$, m. p. 151°, and benzoic acid after three months. Dibromodiphenacylsulphone forms a *dioxime*, $C_{16}H_{14}O_4N_2Br_2S$, m. p. 184°, needles, by boiling with hydroxylamine hydrochloride (two equivalents) and sodium carbonate, and an *oxime*, $C_{16}H_{13}O_4NBr_2S$, m. p. 158°, white needles, by boiling with alcohol and hydroxylamine hydrochloride ; isomeric oximes cannot be isolated.

The behaviour of the oximes and the dioximes of diphenacylsulphone has been partly described by Fromm and Flaschen. The dioxime, m. p. 204°, has the *syn.*-configuration (see below). It yields only an acetyl derivative with acetic anhydride, but by treatment with benzoyl chloride and sodium hydroxide is converted into a *dibenzoyl* derivative, $C_{30}H_{24}O_6N_2S$, m. p. 150°. The *anti*-dioxime has m. p. 209°, not 190°, as stated previously; it forms a *diacetyl* derivative, $C_{20}H_{20}O_6N_2S$,

m. p. 152°, and a *dibenzoyl* derivative, $C_{30}H_{24}O_6N_2S$, m. p. 168°. Its *anti*-configuration is proved by the behaviour of the dioxime with phosphorus pentachloride in boiling ether, whereby, after treatment with water, a *substance*, $C_{16}H_{16}O_4N_2S$, m. p. 215°, is obtained, which must be *sulphonediacetanilide*, $SO_2(CH_2 \cdot CO \cdot NHPh)_2$, since it is decomposed into aniline and sulphuric and acetic acids by aqueous sodium hydroxide. Consequently the dioxime, m. p. 204°, must have the *syn.*-configuration, since the dioxime-anhydride, m. p. 167°, being formed from each of the phenacylsulphoneoximes, must have the *amphi*-configuration.

The configurations of the diphenacylsulphoneoximes follow from the preceding. The *syn.*-dioxime can only result from the *syn.*-oxime; the latter, therefore, must be the oxime, m. p. 144°, since this yields the *syn.*-dioxime by treatment with hydroxylamine hydrochloride and calcium carbonate. The oxime, m. p. 173°, must therefore have the *anti*-configuration.

syn.-Diphenacylsulphonedioxime is unchanged by rapid treatment with phosphorus pentachloride and ether. When the mixture is kept for many days, it yields, after treatment with water, a *substance*, $C_{16}H_{13}O_2N_2Cl_3S$, m. p. 174°, yellow crystals, which is probably trichlorodiphenacylsulphonedioxime or its transformation product, trichlorosulphonediacetanilide; the substance, which can also be obtained from the *anti*-dioxime, is receiving further examination.　C. S.

Preparation of Condensation Products from Phenol-sulphonic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 260379).—An account of the preparation of *compounds*, colourless powders, soluble in water, which are obtained by heating a mixture of *o*- and *p*-phenolsulphonic acids during twenty-four to seventy-two hours at 130—140° under 20 mm. with condensing agents, such as phosphorus trichloride or thionyl chloride.　F. M. G. M.

α-Hydroxy-γ-phenylcrotonic Acid. J. BOUGAULT (*Compt. rend.*, 1913, **157**, 377—379).—The author puts forward an alternative constitution for the γ-hydroxyphenylcrotonic acid obtained from the α-hydroxy-acid by boiling in aqueous solution with oxalic acid (compare this vol., i, 727). From the behaviour of the new isomeride he is unable to decide between the two formulæ:

(I.) $HO \cdot CPh:CH \cdot CH_2 \cdot CO_2H$　(II.) $HO \cdot CHPh \cdot CH:CH \cdot CO_2H$,

but is now inclined to support formula II, by reason of the behaviour of the acid on oxidation with potassium permanganate. Further, he notes that the original transformation is reversible.　W. G.

Isomerisation of the α-Hydroxy-βγ-unsaturated Acids to γ-Ketonic Acids. J. BOUGAULT (*Compt. rend.*, 1913, **157**, 403—405. Compare Thiele, A., 1902, i, 152; Erlenmeyer, A., 1904, i, 1015).—The author considers that the transformation of α-hydroxyphenyl-crotonic acid into *p*-benzoylpropionic acid takes place in two stages, namely: $CHPh:CH \cdot CH(OH) \cdot CO_2H \longrightarrow HO \cdot CHPh \cdot CH:CH \cdot CO_2H \longrightarrow COPh \cdot CH_2 \cdot CH_2 \cdot CO_2H$.

The first stage has already been shown to take place under the

influence of dilute acids (compare preceding abstract), and since the second step can be brought about equally well by acids and alkalis, the intermediate formation of lactones (compare Thiele and Erlenmeyer, *loc. cit.*) is not necessary.   W. G.

Action of Light on Esters of α-Cyanocinnamylideneacetic Acid. II. MARIE REIMER and ELEANOR KELLER (*Amer. Chem. J.*, 1913, **50**, 157—171).—In continuation of previous work (A., 1911, i, 447), the authors have examined the behaviour of the methyl, ethyl, propyl, *iso*propyl, and *iso*butyl esters of α-cyanocinnamylideneacetic acid on exposure to light, both in the solid condition and also in solution. Without solvent all the esters polymerise to a dimeric form, the reaction being practically quantitative, except in the case of the stable ethyl ester, which is considerably oxidised. In alcoholic solution only the methyl ester undergoes polymerisation ; the ethyl ester is transformed into an unstable isomeride, whilst the remaining esters undergo slight oxidation. Similar results were obtained in benzene solution. The behaviour of the isomeric ethyl and *iso*butyl esters has also been studied. On exposure to light without solvent, the isomeric ethyl esters polymerise to dimeric forms, which are not identical but structurally isomeric (compare *loc. cit.*) ; at the same time the stable form is partly oxidised, whilst the unstable form is not.

In benzene and alcoholic solution the stable ethyl ester is transformed into the unstable isomeride ; the reverse reaction does not take place. The isomeric *iso*butyl esters behave in a similar manner.

From these results the conclusion is drawn that the action of light on ethylenic compounds is determined, not only by the nature of the groups, but also by the spatial configuration of the molecule.

The anomalous behaviour of the cinnamylidene compounds described by Stobbe (this vol., i, 177) may be explained on the assumption that in this series, compounds of different configuration were compared.

The unstable ethyl α-cyanocinnamylideneacetate crystallises in flat, straw-coloured needles, m. p. 113°.

Propyl α-cyanocinnamylideneacetate, prepared by the condensation of cinnamaldehyde with propyl cyanoacetate by means of potassium propyloxide in propyl-alcoholic solution, forms long, flat, orange crystals, m. p. 107°, and is converted by light into *propyl* 1 : 3-*diphenylcyclobutane-2 : 4-di-α-cyanoacrylate,*

$$CO_2Pr^a \cdot C(CN):CH \cdot HC \begin{matrix} CHPh \\ CHPh \end{matrix} CH \cdot CH:C(CN) \cdot CO_2Pr^a,$$

which crystallises in white needles, m. p. 107—108°, and is oxidised by potassium permanganate in acetone solution to α-truxillic, benzoic and oxalic acids.

iso*Propyl α-cyanocinnamylideneacetate,* prepared in a similar manner, forms lemon-yellow plates, m. p. 111—112°, and on exposure to light yields *isopropyl* 1 : 3-*diphenylcyclobutane-2 : 4-di-α-cyanoacrylate,* crystallising in needles, m. p. 136°. The stable form of iso*butyl α-cyanocinnamylideneacetate,* prepared by esterifying the acid by the hydrogen chloride method, forms yellow plates, m. p. 114°, and is converted by light into iso*butyl* 1 : 3-*diphenylcyclobutane-2 : 4-di-α-cyanoacrylate,* crystallising in glistening, white needles, m. p. 123°.

The unstable iso*butyl* ester is prepared by the condensation of cinnam-aldehyde with *iso*butyl cyanoacetate. It forms yellow plates, m. p. 110—111°, and by boiling with an *iso*butyl-alcoholic solution of hydrogen chloride is transformed into the stable form. On exposure to light, it polymerises to a dimeric form, $C_{32}H_{34}O_4N_2$, m. p. 114—115°, the constitution of which has not yet been established. F. B.

Phototropy. II. FERDINANDO GRAZIANI and F. BOVINI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 32—41. Compare this vol., i, 984).— The hydrazones described in the present paper of the type

R'R''N·N:CHR

are not phototropic, resembling in this respect those of the type R'R'N·N:CHR previously investigated. The phenomenon is there-fore associated only with hydrazones of the type R'NH·N:CHR, and these must not contain a substituent in the ortho-position of the nucleus of the group R'. The explanation of the phototropy of the hydrazones would then be the mobility of the hydrazinic hydrogen atom, which is displaced to the ortho-position of the nucleus of the group R' by waves of short length, whilst those of great length, including those of heat, reproduce the original, stable form of the hydrazone. Of the hydrazones mentioned in this paper, the following have not previously been prepared:

Cuminaldehydephenylmethylhydrazone, MePhN·N:CH·C₆H₄·CHMe₂, forms pale yellow needles, m. p. 54°.

Cinnamaldehydephenylmethylhydrazone, MePhN·N:CH·CH:CHPh, crystallises in intensely yellow needles, m. p. 114°.

Salicylaldehydephenylmethylhydrazone has m. p. 74° (Labhardt and V. Zembruski, A., 1900, i, 125, gave 71°).

Piperonaldehydephenylmethylhydrazone has m. p. 88° (Goldschmidt, A., 1897, i, 54, gave 85°).

p-*Tolualdehydephenylmethylhydrazone,* MePhN·N:CH·C₆H₄Me, crys-tallises in soapy, yellowish-green leaflets, m. p. 122°.

Vanillinphenylmethylhydrazone, MePhN·N:CH·C₆H₄(OH)·OMe, forms colourless needles, m. p. 122°.

Cinnamaldehydephenylbenzylhydrazone,

CH₂Ph·NPh·N:CH·CH:CHPh,

is a lemon-yellow, crystalline powder, m. p. 167—168°.

Piperonalphenylbenzylhydrazone, CH₂Ph·NPh·N:CH·C₆H₃:O₂:CH₂, forms pale yellow needles, m. p. 124°.

p-*Tolualdehydephenylbenzylhydrazone,* CH₂Ph·NPh·N:CH·C₆H₄Me, crystallises in colourless, silky needles, m. p. 123—124°.

Phenyl-β-naphthylhydrazine may be prepared by reducing the cor-responding nitrosoamine with zinc and acetic acid.

Benzaldehydephenyl-β-naphthylhydrazone, C₁₀H₇·NPh·N:CHPh, forms yellow needles, m. p. 92—93°.

Anisaldehydephenyl-β-naphthylhydrazone,

C₁₀H₇·NPh·N:CH·C₆H₄·OMe,

crystallises in almost colourless, prismatic needles, m. p. 116—117°.

Cuminaldehydephenyl-β-naphthylhydrazone,

C₁₀H₇·NPh·N:CH·C₆H₄·CHMe₂,

forms colourless needles, m. p. 118°.

Cinnamaldehydephenyl-β-naphthylhydrazone,
$$C_{10}H_7 \cdot NPh \cdot N : CH \cdot CH : CHPh,$$
forms pale yellow, acicular crystals, m. p. 156°.

p-*Tolualdehydephenyl-β-naphthylhydrazone* forms yellow, acicular crystals, m. p. 154°.　　　　　　　　　　　　　　　　　R. V. S.

Reduction of Aromatic Ketones. JACOB BÖESEKEN and W. D. COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 91—99).—The authors have made an approximate quantitative study of the reduction of benzophenone by zinc dust and aluminium amalgam in neutral, faintly acid, faintly alkaline, and strongly alkaline alcoholic solutions. For this purpose, quantities of 5 grams of benzophenone were boiled under reflux for definite intervals, with the requisite amount of reducing agent in 50 c.c. of 80% alcohol, filtered hot, made up to 100 c.c., and shaken at 25° for a day. Benzopinacone, being practically insoluble, was then filtered off, if produced at all, and some of the filtrate was evaporated and the residue weighed and examined.

In a neutral solution, zinc dust had no action, but aluminium amalgam produced 32% of pinacone and 68% of pure benzhydrol. In a very faintly acid solution, in a current of carbon dioxide or in presence of ammonium chloride, zinc dust gave rise exclusively to the pinacone. In acetic acid solution both metals produced the pinacone, together with some pinacoline and diphenylmethane, but no benzhydrol. In presence of free ammonia the product was almost exclusively the hydrol, although a small amount of the pinacone was obtained. In a strongly alkaline solution the sole product with zinc dust was benzhydrol (compare Montagne, A., 1907, i, 14), whilst aluminium and magnesium amalgams and sodium gave, in addition, traces of diphenylmethane.

The chief controlling factor is therefore the reaction of the medium. As long as it is acid the pinacone is the sole product, but as soon as hydroxyl ions are present the hydrol appears. In the case of aluminium amalgam in aqueous alcohol it is assumed that a slight excess of these ions occurs at the surface of the metal. As the excess of hydroxyl ions increases, the pinacone can no longer exist, since it is easily converted into a mixture of benzophenone and benzhydrol,
$$[Ph_2COH]_2 \longrightarrow Ph_2CH \cdot OH + Ph_2CO.$$
The first product of the reduction is assumed to be, in all cases, the half-pinacone, Ph_2COH; this would polymerise at once to the pinacone, which would remain unchanged, unless the concentration of hydroxyl ions were such that it would be resolved into the hydrol and the ketone with appreciable velocity. In alkaline solution the half-pinacone might also be reduced directly to the hydrol, but the above assumption would account for the occurrence of a little pinacone in solutions with very low hydroxyl-ion concentration.
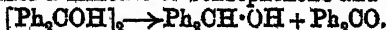
The latter point was verified by the reduction of several substituted benzophenones by means of aluminium amalgam in 80% alcohol. The methoxy- and methyl groups appear to favour the formation of pinacone, but halogens in the nucleus, and especially a number of them, have the opposite effect; thus *pp'*-dichlorobenzophenone gave 96% of hydrol and 4% of pinacone. In dilute acetic acid solution with zinc

dust, however, it gave a quantitative yield of *tetrachlorobenzopinacone*, $C_{26}H_{18}O_2Cl_4$, m. p. 180°.   J. C. W.

Action of Magnesium Phenyl Bromide on Di-α-bromoiso-propyl Ketone. (Mlle.) ANNA I. UMNOVA (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 881—884).—From a study of the products obtained by the interaction of magnesium methyl bromide (or iodide) and di-α-bromoisopropyl ketone (this vol., i, 7), it is supposed that the reaction is represented by the equation :

$$CMe_2Br\cdot CO\cdot CMe_2Br + 2MgMeX =$$
$$CH_3X + MgBrX + CMe_3\cdot CO\cdot CMe_2\cdot MgBr,$$

the action of water then yielding *iso*propyl *tert.*-butyl ketone. This supposition is supported by the liberation of a gas burning with a green flame when methyl bromide is employed, and by the formation of silver iodide when the ethereal extract of the products obtained with methyl iodide is treated with silver nitrate ; the formation of methyl iodide was not, however, directly proved.

If, however, magnesium phenyl bromide is used in the reaction in place of the magnesium methyl compound, bromobenzene is found to be liberated. In one case, the complex magnesium ketonic compound was treated with water so as to yield α-phenyl*iso*propyl *iso*propyl ketone, and in another with carbon dioxide to give the corresponding β-ketonic acid.

α-*Phenyliso*propyl *iso*propyl *ketone*, $CPhMe_2\cdot CO\cdot CHMe_2$, b. p. 118—119°/12 mm., 243—244°/760 mm., could not be obtained quite free from diphenyl. Its *bromo*-derivative, $C_{13}H_{17}OBr$, forms stout prisms, m. p. 64—65°, apparently containing alcohol of crystallisation, and has the normal molecular weight in freezing benzene.

The *ketonic acid*, $CPhMe_2\cdot CO\cdot CMe_2\cdot CO_2H$, m. p. 90—91° (decomp.), exhibits marked association in freezing benzene. Its *silver* salt was analysed.   T. H. P.

Condensation Products of *m*-Methoxybenzaldehyde. HUGO BAUER and P. VOGEL (*J. pr. Chem.*, 1913, [ii], **88**, 329—342).—It has been shown previously (A., 1903, i, 479 ; 1904, i, 385 ; 1911, i, 881) that the introduction of alkyloxy-groups in the ortho- and para-position of the benzene nucleus in compounds of the type

$$CHPhBr\cdot CHBr\cdot R$$
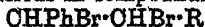
is accompanied by a marked increase in the reactivity of the bromine atom adjacent to the aromatic group; the bromine atom is readily replaced by alkyloxy-groups when the dibromides are boiled in alcoholic solution.

The reactivating influence of the alkyloxy-groups is apparently confined to the ortho- and para-positions, for the dibromides of *m*-methoxy-styryl methyl ketone and phenyl *m*-methoxystyryl ketone may be boiled with alcohol without undergoing change.

m-*Methoxystyryl methyl ketone*, $OMe\cdot C_6H_4\cdot CH\!:\!CH\cdot COMe$, obtained as an oil, b. p. 173°/8 mm., by the condensation of *m*-methoxybenz-aldehyde with acetone in the presence of aqueous sodium hydroxide, forms a *semicarbazone*, slender, yellow needles, m. p. 197—198°, and a yellow, crystalline *phenylhydrazone*, m. p. 116—117°, which decomposes when kept and is converted by boiling in glacial acetic acid solution

into 1-*phenyl*-5-m-*methoxyphenyl*-3-*methylpyrazoline*,

$$\begin{array}{c} CMe \cdot CH_2 \\ N\!\!-\!\!-\!\!NPh \end{array}\!\!\!>\!\!CH \cdot C_6H_4 \cdot OMe,$$
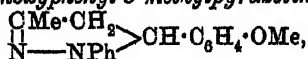
m. p. 93—94°. It reacts with bromine (2 mols.), yielding *αβ-6-tri-bromo-α-3-methoxyphenylbutan-γ-one*, OMe·C_6H_3Br·CHBr·CHBr·COMe. This forms slender, white crystals, m. p. 112°, and when heated with pyridine loses hydrogen bromide with the formation of *β-6-dibromo-α-3-methoxyphenyl-Δ^α-buten-γ-one*, OMe·C_6H_3Br·CH:CBr·COMe, which crystallises in extremely slender, colourless, down-like needles, m. p. 64°. The position of the bromine atom in the benzene nucleus of the preceding compounds has been established by the formation of 6-bromo-3-methoxybenzoic acid (Pschorr and others, A., 1912, i, 775) on oxidising the dibromo-compound with aqueous permanganate.

Phenyl m-*methoxystyryl ketone*, OMe·C_6H_4·CH:CH·COPh, prepared by the condensation of *m*-methoxybenzaldehyde and acetophenone in alcoholic solution by means of sodium hydroxide has b. p. 247°/12 mm., m. p. 65°, and is converted by phenylhydrazine in boiling alcoholic solution into 1 : 3-*diphenyl*-5-m-*methoxyphenylpyrazoline*, which crystallises in slender, green needles, m. p. 98°, yields green, fluorescent solutions in alcohol and acetone, and is oxidised by aqueous potassium permanganate to 1 : 3-*diphenyl*-5-m-*methoxyphenylpyrazole*, $C_{22}H_{18}ON_2$, crystallising in large, yellow needles, m. p. 140°.

It reacts with bromine in glacial acetic acid solution, yielding *αβ-6-tri-bromo - β - 3 - methoxyphenylpropiophenone* (*phenyl αβ - 6-tribromo-β-3-methoxyphenylethyl ketone*), OMe·C_6H_3Br·CHBr·CHBr·COPh. This forms stout, colourless crystals, m. p. 140°, and is oxidised by potassium permanganate to 6-bromo-3-methoxybenzoic acid. When heated with pyridine or alcoholic ammonia, it is converted into *phenyl α-6-dibromo-3-methoxystyryl ketone*, OMe·C_6H_3Br·CH:CBr·COPh, which forms slender needles, m. p. 105°. With alcoholic sodium ethoxide it forms *phenyl α-6-dibromo-β-ethoxy-β-3-methoxyphenylethyl ketone*,

$$OMe \cdot C_6H_3Br \cdot CH(OEt) \cdot CHBr \cdot COPh,$$
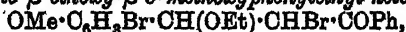
m. p. 109—110°.

Ethyl m-*methoxybenzylidenemalonate*, OMe·C_6H_4·CH:C(CO$_2$Et)$_2$, prepared by maintaining a mixture of *m*-methoxybenzaldehyde and ethylmalonate, containing a little pyridine, for eight days at the ordinary temperature has m. p. 47°, b. p. 204—206°/10 mm., and is hydrolysed by aqueous sodium hydroxide to the corresponding *acid*, m. p. 163°, which forms a crystalline *barium* and amorphous *silver* salt, and reacts with bromine (1 mol.) in ethereal solution, yielding *α-bromo-α-m-methoxyphenylmethylenemalonic acid*, OMe·C_6H_4·CBr:C(CO$_2$H)$_2$, slender, yellow needles, m. p. 188°.

The *ethyl* ester of the last-mentioned acid is obtained as a viscid oil, b. p. 208°/10 mm., by the addition of bromine to ethyl *m*-methoxybenzylidenemalonate in glacial acetic acid.

m-Methoxybenzylidenemalonic acid reacts with bromine (2 mols.) in acetic acid solution, yielding *α-6-dibromo-α-3-methoxyphenylmethylene-malonic acid*, OMe·C_6H_3Br·CBr:C(CO$_2$H)$_2$, slender, pale yellow needles, m. p. 167°. When heated at 180°, it loses carbon dioxide with the formation of *m*-methoxycinnamic acid, m. p. 117° (compare Tiemann and Ludwig, A., 1883, 188), which is successively converted by the

action of bromine in glacial acetic acid solution int₃ β-bromo-m-*methoxycinnamic acid*, slender, colourless needles, m. p. 186°, and β-6-*dibromo-3-methoxycinnamic acid*, OMe·C₆H₃Br·CBr:CH·CO₂H, white needles, m. p. 160°.

6-Bromo-3-methoxybenzoic acid is readily prepared by shaking m-methoxybenzaldehyde with water and the theoretical amount of bromine.

If excess of bromine is used, it is accompanied by a *dibromo-m-methoxybenzoic acid*, which crystallises in slender, felted needles, m. p. 201—202°, and is separated from the monobromo-acid by taking advantage of its sparing solubility in water.   F. B.

Some Acetylenic Compounds. ÉMILE ANDRÉ (*Ann. Chim. Phys.*, 1913, [viii], **29**, 540—596).—The paper is mainly a résumé of work previously abstracted (A., 1910, i, 563; 1911, i, 269, 277, 545; 1912, i, 628). The following points are, however, new.

Unsuccessful attempts have been made to prepare phenylpropinene, CH₂Ph·C⋮CH, by the elimination of hydrogen bromide from allylbenzene dibromide.

Phenylbutinene has b. p. 189—191°/760 mm., D⁰ 0·9375.

iso*Heptylene*, b. p. 84—85°/762 mm., D⁰ 0·7087, is obtained by the addition of an ethereal solution of allyl iodide to a solution of magnesium *iso*butyl chloride in the same solvent. It unites with bromine, yielding a *dibromide* which, when heated with solid potassium hydroxide at about 130°, is converted into iso*heptinene*, CHMe₂·CH₂·CH₂·C⋮CH, b. p. 92—93°, D⁰ 0·7515.

α-*Propionyl-δ-phenylbutinene*, CH₂Ph·CH₂·C⋮C·COEt, is prepared by the gradual addition of a suspension of the potassium compound of δ-phenylbutinene in benzene to a solution of propionyl chloride in benzene. It is a pale yellow liquid, b. p. 162—163°/15 mm., D⁰ 1·0156; the *piperidyl* compound has m. p. 44°.

Propionylisoheptinene, b. p. 100—101°/15 mm., D⁰ 0·8902, is obtained in a similar manner, the benzene, however, being replaced by anhydrous ether.

ε-*Diethylamino-β-methyl-Δᵋ-nonen-η-one*, b. p. 163°/13 mm., is obtained by mixing its constituents at a low temperature.

α-*Propionyl-δ-phenylbutan-β-one*, CH₂Ph·CH₂·CO·CH₂·COEt, has b. p. 166°/13 mm., D⁰ 1·0460, and α-*propionylisoheptan-β-one*,

$$CHMe_2·CH_2·CH_2·CO·CH_2·COEt,$$

b. p. 106°/14 mm., D⁰ 0·9262.

Ethylenic β-substituted amino-ketones react with hydroxylamine in a complex manner. Thus diethylaminobenzoylstyrene yields a small quantity of 3 : 5-diphenyl*iso*oxazole, O⟨N⁼⁼CPh / CPh:CH , m. p. 142°, together with two other *substances*, one of which has m. p. 163°.

Hexoylphenylacetylene and *iso*valerylphenylacetylene react with hydroxylamine to yield 5-*phenyl-3-amylisooxazole*, m. p. 25—26°, b. p. 186—187°/13 mm., and 5-*phenyl-3-isobutylisooxazole*, b. p. 172°/13 mm., respectively, neither of which regenerates hydroxylamine when heated with dilute hydrochloric acid.

3-Phenyl-5-*amylpyrazole*, plates, m. p. 77—78°, is formed by the action of hydrazine on hexoylphenylacetylene.

Reduction of ethylenic β-substituted amino-ketones by sodium or sodium amalgam in alcoholic solution, or by aluminium amalgam in neutral solution, causes a quantitative separation of the amine. A regular hydrogenation of the remainder of the molecule has not yet been achieved.   H. W.

Action of Ethyl Oxalate on Cyclic Ketones. ARTHUR KÖTZ and J. MEYER (*J. pr. Chem.*, 1913, [ii], **88**, 261—272).—In previous papers (A., 1906, i, 88, 666, 667, 668), Kötz and others have shown that cyclic ketones condense with ethyl oxalate under the influence of sodium alkyloxides, yielding ketonic esters of the formula

$$R\!\!<^{CO}_{CH\cdot CO\cdot CO_2Et}\cdot$$
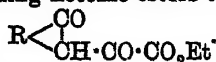
It is now found that in the case of certain derivatives of *cyclo*-hexanone, alcohol may be eliminated from the ketonic esters during the condensation, resulting in the formation of lactones derived from the following formulæ:

$$\begin{matrix} CH_2\cdot CH{=}C\cdot O\cdot CO \\ CH_2\cdot CH_2\cdot CH{-}CO \end{matrix}\ or\ \begin{matrix} CH_2\cdot CH{=}C\cdot O\cdot CO \\ CH_2\cdot CH_2\cdot C{=}C\cdot OH \end{matrix}\cdot$$
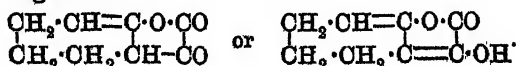
One example of the formation of a lactone of this type has already been recorded (this vol., i, 179).

From the authors' results it would appear that ketonic esters are produced when the time during which the reaction is allowed to proceed is short and the temperature low, whilst a high temperature and a more prolonged action favour the formation of lactones.

Ethyl suberone-2-*oxalate* (*ethyl* 2-*cycloheptanonylglyoxylate*), prepared from *cyclo*heptanone, ethyl oxalate, and alcoholic sodium ethoxide, has b. p. 146—148°/13 mm.

3-Methyl-Δ²-*cyclohexen*-2-*ol*-1-*glyoxylolactone* (this vol., i, 179) yields with acetic anhydride an *acetyl* derivative,

$$\begin{matrix} CH_2\cdot CMe{:}C\cdot O\cdot CO \\ CH_2\cdot CH_2\cdot C{=}C\cdot OAc \end{matrix},$$
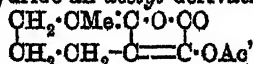
m. p. 78°.

The methyl derivative of the lactone (*loc. cit.*) is hydrolysed by aqueous potassium hydroxide (1 mol.) to 3-*methyl*cyclohexan-2-onylidene-methoxyacetic acid, m. p. 139°, $CH_2\!\!<^{CHMe\cdot CO}_{CH_2-CH_2}\!\!>C{:}C(OMe)\cdot CO_2H$ or

$CH_2\!\!<^{CMe{:}C(OH)}_{CH_2-CH_2}\!\!>C{:}C(OMe)\cdot CO_2H.$
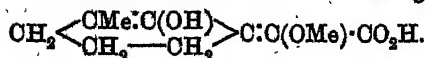
2-Methoxy*cyclo*hexanone condenses with ethyl oxalate, yielding 3-*methoxy*-Δ²-*cyclohexen*-2-*ol*-1-*glyoxylolactone*,

$$\begin{matrix} CH_2\cdot C(OMe){:}C\cdot O\cdot CO \\ CH_2\cdot CH_2{-}{-}CH{-}CO \end{matrix}\ or\ \begin{matrix} CH_2\cdot C(OMe){:}C\cdot O\cdot CO \\ CH_2\cdot CH_2{-}{-}C{=}C\cdot OH \end{matrix},$$
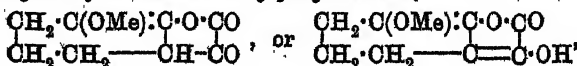
which has m. p. 51°.

3:6-*Dimethyl*-Δ²-*cyclohexen*-2-*ol*-1-*glyoxylolactone*, from 1:4-dimethyl-*cyclo*hexan-3-one, has m. p. 158—159°.

6-Methyl-3-isopropyl-Δ²-cyclohexen-2-ol-1-glyoxylolactone,

$$CH_2\cdot CMe\vdots C\!\!-\!\!CO$$
$$CH_2\cdot OPr^\beta\vdots C\cdot O\cdot CO \text{ ,}$$
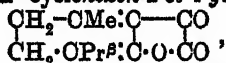
prepared from menthone, ethyl oxalate, and sodium in the presence of light petroleum, has m. p. 142·5° (decomp.), and decomposes on exposure to air.

In addition to ketonic esters and lactones, the condensation of ethyl oxalate with *cyclo*hexanone and its methyl derivatives gives rise to triketones or pyrone derivatives, which are found in the higher boiling fractions of the condensation product.

Thus, the condensation of 2-methyl*cyclo*hexanone and ethyl oxalate yields, as a by-product, *bis*-3-*methyl*cyclohexan-2-onyl *ketone*,

$$CH_2{<}^{CHMe\cdot CO}_{CH_2\!-\!CH_2}{>}OH\cdot CO\cdot OH{<}^{CO\cdot CHMe}_{CH_2\!-\!CH_2}{>}CH_2,$$
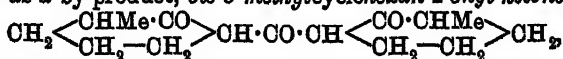
which has b. p. 170°/13 mm., and gives a reddish-violet coloration with ferric chloride.

Biscyclohexan - 2 - onyl ketone, from *cyclo*hexanone, has b. p. 181°/14 mm.

3-Methyl*cyclo*hexanone yields the *pyrone* derivative, m. p. 121°,

$$CHMe\cdot OH_2\cdot C\!-\!O\!-\!C\cdot OH_2\cdot CHMe$$
$$OH_2\cdot OH_2\!-\!C\cdot CO\cdot C\cdot OH_2\cdot OH_2 \text{ ; the } pyrone \text{ derivative from 4-methyl-}$$

*cyclo*hexanone has m. p. 91°.

The formation of the above-mentioned products is probably due to the intermediate formation of tetraketones of the type:

$$CH_2{<}^{CH_2\!-\!CO}_{CH_2\cdot CH_2}{>}OH\cdot CO\cdot CO\cdot OH{<}^{CO\!-\!CH_2}_{CH_2\cdot CH_2}{>}CH_2,$$
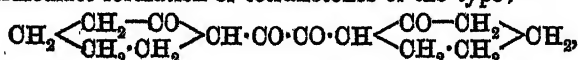
by the condensation of one molecule of the ester with two molecules of the ketone, the tetraketone being subsequently converted into the triketone and pyrone derivatives by loss of carbon monoxide and water. F. B.

Unsaturated β-Diketones. I. HUGH RYAN and JOHN M. DUNLEA (*Proc. Roy. Irish Acad.*, 1913, **32**, 1—8).—Some typical unsaturated β-diketones have been prepared by condensing cinnamic esters with saturated ketones in presence of sodium or sodamide. All attempts to prepare similar compounds by condensing acetic and benzoic esters with unsaturated ketones have, however, failed, and consequently the chief aim of the research, the formation of the parent substance of curcumin, $CH_2(CO\cdot OH\vdots CHPh)_2$, from a cinnamic ester and styryl methyl ketone, could not be realised.

For the preparation of *a-phenyl-Δª-hexene-yε-dione,*

$$OHPh\vdots OH\cdot CO\cdot OH_2\cdot COMe,$$

sodium wire was added during the course of some hours to a cold mixture of acetone and methyl cinnamate, and the sodium salt of the diketone was dissolved in water and decomposed by carbon dioxide. The compound crystallises in faintly yellow needles, has m. p. 83—84°, gives a yellow solution in concentrated sulphuric acid, and a red coloration with alcoholic ferric chloride, and dyes mordanted wool. On heating with hydroxylamine hydrochloride in alcohol, it yields

3-*styryl*-5-*methyl*isooxazole, $CHPh{:}CH{\cdot}C{<}^{CH{:}CMe}_{N—O}$, which forms pearly plates from alcohol or colourless needles from light petroleum, m. p. 88°. *αε-Diphenyl-Δ*α-*pentene-*γε-*dione*, $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}COPh$, from acetophenone and ethyl cinnamate in the presence of sodamide, forms long, pale yellow needles, m. p. 109°, and yields 5-*phenyl*-3-*styryl*isooxazole, $CHPh{:}CH{\cdot}C{<}^{CH{:}CPh}_{N—O}$, in small, colourless needles, m. p. 137—138°.

*α-Phenyl-Δ*α-*heptene-*γε-*dione*, $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}COEt$, from methyl cinnamate and methyl ethyl ketone, requires a stronger acid than carbon dioxide for the decomposition of its sodium compound. It forms small, colourless prisms, which soften at 154° and melt to a yellow liquid at 161—163°. Similarly, *α-phenyl-Δ*α-*isooctene-*γε-*dione*, $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CHMe_2$, crystallises in thin plates which are probably rhombic, and softens at 165° and melts to a yellow liquid at 173—175°. These diketones are soluble in potassium hydroxide, but do not give coloured solutions in sulphuric acid or colorations with ferric chloride, nor do they dye mordanted wool. That their constitution is not represented by the alternative formulæ was proved by methylating α-phenyl-Δα-hexene-γε-dione, when it was found that *α-phenyl-δ-methyl-Δ*α-*hexene-*γε-*dione*, $CHPh{:}CH{\cdot}CO{\cdot}CHMe{\cdot}COMe$, was not identical with the above α-phenyl-Δα-heptene-γε-dione, but formed long, pale yellow needles, m. p. 88—89°, and gave a dark brown coloration with alcoholic ferric chloride, a yellow solution in sulphuric acid, and a pale brown colour to wool mordanted with iron.

<div align="right">J. C. W.</div>

Unsaturated β-Diketones. II. HUGH RYAN and JOSEPH ALGAR (*Proc. Roy. Irish Acad.*, 1913, **32**, 9—16).—Although unsaturated ketones did not yield definite compounds on condensation with acetic or benzoic esters (compare preceding abstract), such a result has been attained with the oxalic esters. *Methyl* αγ-*diketo-*ε-*phenyl-Δ*δ-*hexenoate* (*methyl benzylideneacetoneoxalate*),

<div align="center">$CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Me$,</div>
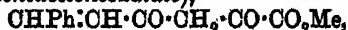
from styryl methyl ketone and methyl oxalate in the presence of sodium, forms pale yellow, acicular prisms, m. p. 70° (compare the ethyl ester, Schiff and Gigli, A., 1898, i, 490). It gives a yellow solution in potassium hydroxide, an orange solution in concentrated sulphuric acid, and a yellow solution with greenish fluorescence in alcohol. Ferric chloride imparts a dark red colour to an alcoholic solution, and the substance dyes wool orange-red or brown, according to the mordant employed. αγ-*Diketo-*ε-*phenyl-Δ*δ-*hexenoic acid*, $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$, may readily be obtained by hydrolysis of the esters, in pale yellow needles, m. p. 139—140°. When the methyl ester is heated with hydroxylamine hydrochloride in methyl alcohol, *methyl* 3-*styryl*isooxazole-5-*carboxylate*,

<div align="center">$CHPh{:}CH{\cdot}C{<}^{CH{:}C{\cdot}CO_2Me}_{N—O}$,</div>
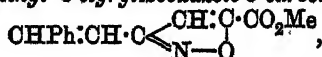
is formed in long, colourless needles, m. p. 142—143°. When ethyl

alcohol is employed, however, a transformation occurs, and the *ethyl ester* is produced, in colourless crystals, m. p. 111°. The free *acid*, $C_{12}H_9O_3N$, is white, and has m. p. 190—192°. The above methyl ester also absorbs bromine, yielding *methyl δε-dibromo-aγ-diketo-ε-phenylhexoate*, CHPhBr·CHBr·CO·CH$_2$·CO·CO$_2$Me, in almost colourless prisms, m. p. 134°.

Similar compounds were obtained by condensing *p*-methoxystyryl methyl ketone with methyl oxalate. *Methyl aγ-diketo-ε-p-methoxyphenyl-Δδ-hexenoate*, OMe·C$_6$H$_4$·CH:CH·CO·CH$_2$·CO·CO$_2$Me, forms yellow needles, m. p. 127·5°, and with bromine yields *methyl δε-dibromoaγ-diketo-ε-p-methoxyphenylhexoate*, $C_{14}H_{14}O_5Br_2$, in pale yellow needles, m. p. 106—108° (decomp.). The free *acid* crystallises with water in bright yellow, slender needles, whilst the anhydrous substance is deep orange, and has m. p. 150—151°. *Ethyl 3-p-methoxystyryl-isooxazole-5-carboxylate*, $C_{15}H_{15}O_4N$, from the above methyl ester with hydroxylamine hydrochloride in ethyl alcohol, forms long, colourless needles, m. p. 76—77°.   J. C. W.

Alkylation of Ketones by means of β-Ketoneoxalic Esters.
ARTHUR KÖTZ and K. BLENDERMANN (*J. pr. Chem.*, 1913, [ii], 88, 257—260).—The method previously employed (this vol., i, 179) to convert 1-methyl*cyclo*hexan-3-one into 1 : 4-dimethyl*cyclo*hexan-3-one is found to be of general application for alkylating both aliphatic and hydroaromatic ketones. It consists in condensing the ketone with ethyl oxalate by means of sodium methoxide or ethoxide, heating the sodium derivative of the resulting ketonic ester (I) with an alkyl haloid, and hydrolysing the product (II) with aqueous alkali hydroxides :

$$R\underset{CH_2}{\overset{CO}{<}} \longrightarrow (I.)\ R\underset{CH·CO·CO_2Et}{\overset{CO}{<}} \overset{R'I}{\longrightarrow}$$

$$(II.)\ R\underset{CR'·CO·CO_2Et}{\overset{CO}{<}} \longrightarrow R\underset{CHR'}{\overset{CO}{<}} + EtOH + H_2C_2O_4.$$
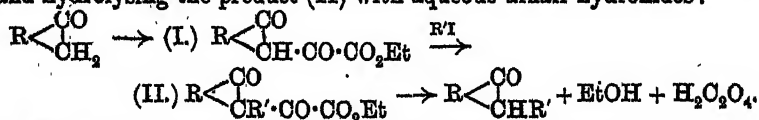
Thus, acetone can be converted into methyl ethyl ketone by condensing it with ethyl oxalate and alcoholic sodium ethoxide, heating the ethyl sodioacetoneoxalate thus formed with methyl iodide, and hydrolysing the resulting methyl derivative with the calculated amount of 10% aqueous sodium hydroxide.

Ethyl 1 : 3-dimethyl*cyclo*hexan-2-onylglyoxylate,

$$CH_2\underset{CH_2-CH_2}{\overset{CHMe·CO}{<}}>CMe·CO·CO_2Et,$$
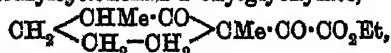
obtained from 1-methyl*cyclo*hexan-2-one, ethyl oxalate, and methyl iodide, yields, on hydrolysis, 1 : 3-dimethyl*cyclo*hexan-2-one (Kötz and Schaeffer, A., 1912, i, 603).

On treatment with ethyl iodide and subsequent hydrolysis, the sodium derivative of ethyl 4-methyl*cyclo*hexan-2-onylglyoxylate, obtained from 1-methyl*cyclo*hexan-3-one and ethyl oxalate, yields 1-*methyl-4-ethylcyclohexan-3-one*, a strongly refractive, colourless liquid, b. p. 81—82°/17 mm., having an odour resembling that of menthone.

4-Benzyl-1-methylcyclohexan-3-one, prepared in a similar manner, using benzyl chloride, has b. p. 176°/15 mm.

Ethyl methylisothujoneoxalate (*ethyl* 1 : 3 : 4-*trimethyl-5-isopropyl-Δ³-*

cyclo*hexen-2-onylglyoxylate*), $\begin{matrix} CMe\text{——}CO \\ CMe\cdot CHPr^\beta \end{matrix}\text{>}$CMe·CO·CO$_2$Et, obtained by
heating the product of the condensation of *iso*thujone and ethyl oxalate
with methyl iodide, has b. p. 183°/11 mm., and is hydrolysed by
aqueous sodium hydroxide to *methyliso*thujone (1 : 3 : 4-*trimethyl*-5-
isopropyl-Δ³-cyclo*hexen-2-one*), $\begin{matrix} CMe\text{——}CO \\ CMe\cdot CHPr^\beta \end{matrix}\text{>}$CHMe, which has b. p.
229—231°, and has also been prepared by the reduction of hydroxy-
methyleneisothujone (Schaeffer, *Diss.*, Göttingen, 1903).   F. B.

**Isolation of Lapachol from the Heart-wood of Avicennia
tomentosa.** KONRAD BOURNOT (*Arch. Pharm.*, 1913, 251, 351—354).
—The residue left after the evaporation of the ethereal extract of the
powdered heart-wood of *Avicennia tomentosa* yields to 3% aqueous
sodium carbonate a substance, lapachol, $C_{15}H_{14}O_3$, m. p. 140—141°,
truncated, yellow plates, which is shown by its m. p., crystalline form,
solubilities, and formation of a diacetyl derivative, m. p. 130°, to be
identical with Paternò's and with Hooker's lapachoic acid (2-hydroxy-
3-ωω-dimethylallyl-α-naphthaquinone).   C. S.

**The Anthraquinone Series. I. Halogenated 2-Amino-
anthraquinones.** WALTER JUNGHANS (*Annalen*, 1913, 399, 316—330).
—1-*Chloro*-2-*acetylaminoanthraquinone*, m. p. 241—242° (corr.), faintly
yellow needles, obtained by the chlorination of 2-acetylaminoanthra-
quinone in acetic acid containing sodium acetate on the water-bath,
yields, by hydrolysis by acids or alkalis, 1-*chloro*-2-*aminoanthraquinone*,
m. p. 237°, orange needles or reddish-brown leaflets. The latter reacts
with *p*-toluenesulphonamide, potassium acetate, and a trace of copper
acetate in boiling amyl alcohol to form 1-*p*-*toluenesulphonylamino*-
2-*aminoanthraquinone*, m. p. 239° (corr.), yellowish-red leaflets. In a
similar manner, 1-chloro-2-acetylaminoanthraquinone yields 1-*p*-*toluene-
sulphonylamino*-2-*acetylaminoanthraquinone*, m. p. 207° (corr.), long
needles. Both of these substances yield 1 : 2-diaminoanthraquinone by
hydrolysis, whereby the constitution of the chloroaminoanthraquinone
is determined.
By treatment with chlorine in warm glacial acetic acid or with
potassium chlorate and concentrated hydrochloric acid in glacial acetic
acid at the ordinary temperature, 2-aminoanthraquinone yields 1 : 3-*di-
chloro*-2-*aminoanthraquinone*, m. p. 231° (corr.), yellowish-brown needles,
which is converted by boiling acetic anhydride into 1 : 3-*dichloro*-
2-*diacetylaminoanthraquinone*, m. p. 199° (corr.), silvery leaflets, and
into 1 : 3-*dichloro*-2-*benzoylaminoanthraquinone*, m. p. 227° (corr.),
faintly yellow needles, by benzoyl chloride in boiling nitrobenzene.
The constitution of 1 : 3-dichloro-2-aminoanthraquinone is proved by
eliminating the amino-group in the usual manner, whereby is obtained
the 1 : 3-*dichloroanthraquinone*, m. p. 203° (corr.), which is produced
from 1 : 3-dichloro-4-aminoanthraquinone by the same method.
Contrary to statements in the literature, the interaction of equal
molecular quantities of 2-aminoanthraquinone and bromine in glacial
acetic acid at the ordinary temperature produces 3-*bromo*-2-*amino*-

anthraquinone hydrobromide, from which the *base,* m. p. 311° (corr.), yellow leaflets, is obtained by boiling with water. 3-Bromo-2-amino-anthraquinone forms an *acetyl* derivative, m. p. 217° (corr.), colourless needles, and a *benzoyl* derivative, m. p. 279° (corr.), colourless needles. Its constitution is proved by deamidation, whereby 2-bromoanthra-quinone is produced, and also by the formation of a thiazole derivative (Ullmann and Junghans, below). By prolonged boiling with glacial acetic and concentrated hydrobromic acids, 1 : 3-dibromo-2-amino-anthraquinone loses the halogen atom in position 1 and yields 3-bromo-2-aminoanthraquinone, m. p. 311° (corr.). C. S.

Preparation of β-Bromoaminoanthraquinones Containing a Bromine Atom in the Next Position to an Amino-group. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 261270 and 261271).— *3-Bromo-2-aminoanthraquinone,* m. p. 305°, as previously obtained (A., 1904, i, 512) had m. p. 267—270°, and the pure substance has now been prepared as follows : 2-aminoanthraquinone (5·8 parts) and 10 parts of 1 : 3-dibromo-2-aminoanthraquinone (A., 1905, i, 797) dissolved in 160 parts of concentrated sulphuric acid are slowly heated with continual stirring to 160°, when a reaction takes place, and after about fifteen minutes at 170° pure 3-bromo-2-aminoanthraquinone sulphate crystallises out ; the same result is obtained if the bases are heated together during ten minutes at 280° in the absence of any solvent.

2-Bromo-1-aminoanthraquinone (A., 1905, i, 910) is obtained in a similar manner from 1-aminoanthraquinone and 2 : 4-dibromo-1-amino-anthraquinone.

1 : 3 : 5 : 7-*Tetrabromo-*2 : 6-*diaminoanthraquinone,* yellowish-brown needles, m. p. above 360°, is prepared by brominating an aqueous suspension of 2 : 6-diaminoanthraquinone, and when molecular proportions of these two bases are heated together at 195° in slightly diluted sulphuric acid during half an hour, they furnish pure 3 : 7-*dibromo-*2 : 6-*diaminoanthraquinone sulphate ;* whilst a mixture of 1 : 5-diamino-and 2 : 4 : 6 : 8-tetrabromo-1 : 5-diamino-anthraquinones gives rise to 2 : 6-dibromo-1 : 5-diaminoanthraquinone (A., 1905, i, 88).

II. States that 3-bromo-2-aminoanthraquinone can be prepared in one operation by dissolving 2-aminoanthraquinone in concentrated sulphuric acid, cooling, and treating with bromine (1 mol.) ; the crude mixture, which contains monobromo-, dibromo-, and unbrominated bases, is then heated at 180—190°, when it furnishes entirely 3-bromo-2-aminoanthraquinone. In a similar manner, 2 : 7-diaminoanthra-quinone when treated with bromine (2 mols.) gives rise to 3 : 6-*dibromo-*2 : 7-*diaminoanthraquinone ;* this compound closely resembles 3 : 7-dibromo-2 : 6-diaminoanthraquinone, but is more readily soluble in organic liquids. F. M. G. M.

The Anthraquinone Series. II. 1 : 3-Dibromo-2-amino-anthraquinone. FRITZ ULLMANN and WALTER JUNGHANS (*Annalen,* 1913, 399, 330—345).—The following reactions illustrate the great mobility, in the presence of a copper salt as catalyst, of the halogen

atom in position 1 in 1 : 3-dibromo-2-aminoanthraquinone (compare Ullmann and Medenwald, this vol., i, 735). By boiling with benzoyl chloride and nitrobenzene, or with benzoic anhydride, 1 : 3-dibromo-2-aminoanthraquinone yields 3-*bromoanthraquinonylphenyloxazole*,

$$C_6H_4 \underset{CO}{\overset{CO}{<}} > C_6HBr \underset{N}{\overset{O}{<}} > CPh,$$
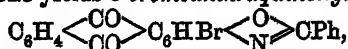
m. p. 325° (corr.), yellow leaflets, which is decomposed by boiling 80% sulphuric acid, forming, after the addition of water, 3-*bromo*-2-*amino*-1-*hydroxyanthraquinone*, m. p. 269°, reddish-brown needles. 1 : 3-*Dibromo*-2-*dibenzoylaminoanthraquinone*, m. p. 233°, yellow needles, is also obtained by the first method of preparing the oxazole derivative.

In a similar manner, 1 : 3 : 5 : 7-tetrabromo-2 : 6-diaminoanthraquinone, by boiling with benzoyl chloride and naphthalene, is converted into the *bisoxazole*,

$$CPh \underset{O}{\overset{N}{<}} > C_6HBr \underset{CO}{\overset{CO}{<}} > C_6HBr \underset{O}{\overset{N}{<}} > CPh,$$
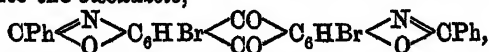
m. p. above 360°, faintly yellow needles.

By boiling with amyl alcohol, anhydrous potassium acetate, a little copper acetate, and *p*-toluenesulphonamide, 1 : 3-dibromo-2-aminoanthraquinone is converted into 3-*bromo*-2-*amino*-1-*p-toluenesulphonylaminoanthraquinone*, $C_{21}H_{15}O_4N_2BrS$, m. p. 237·5° (corr.), yellowish-brown crystals, which yields 3-*bromo*-1 : 2-*diaminoanthraquinone*, m. p. 312° (corr.), dark red crystals, by hydrolysis · with sulphuric acid. By boiling 3-bromo-1 : 2-diaminoanthraquinone with benzaldehyde or 3-bromo-2-amino-1-*p*-toluenesulphonylaminoanthraquinone with benzoyl chloride, the *iminoazole*, $C_6H_4 \underset{CO}{\overset{CO}{<}} > C_6HBr \underset{NH}{\overset{N}{<}} > CPh$, m. p. 292° (corr.),

yellowish-green needles, is obtained, which forms a *hydrochloride*, colourless needles, and a reddish-brown *sodium* salt.

In the presence of anhydrous sodium acetate and a trace of copper acetate, 1 : 3-dibromo-2-aminoanthraquinone is converted by urethane on the water-bath into *bromohydroxyanthriminazole*,

$$C_6H_4 \underset{CO}{\overset{CO}{<}} > C_6HBr \underset{N}{\overset{NH}{<}} > C·OH,$$
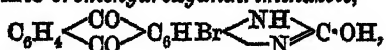
m. p. 370°, yellowish-green needles, and by boiling nitrobenzene into 3 : 3'-*dibromoindanthren*,

$$C_6H_4 \underset{CO}{\overset{CO}{<}} > C_6HBr \underset{NH}{\overset{NH}{<}} > C_6HBr \underset{CO}{\overset{CO}{<}} > C_6H_4,$$

m. p. 515°, indigo-blue needles, and 3-bromo-2-aminoanthraquinone ; the dibromoindanthren forms a blue vat which dyes cotton in blue shades.

1 : 3-Dibromo-2-aminoanthraquinone and boiling benzaldehyde yield a *benzylidene* derivative, $C_{21}H_{11}O_2NBr_2$, m. p. 195° (corr.), yellowish-green needles, which is converted by naphthalene and copper powder at 240—245° into 3 : 3'-*dibromo*-2 : 2'-*dibenzylideneamino*-1 : 1'-*dianthraquinonyl*, $C_{42}H_{22}O_4N_2Br_2$, m. p. 295·5° (corr.), yellow leaflets. By treating the latter in hot nitrobenzene with a little sulphuric acid, or 3-bromo-2-aminoanthraquinone in boiling nitrobenzene with antimony pentachloride, 3 : 3'-*dibromoflavanthren*, $C_{28}H_{10}O_2N_2Br_2$, m. p. 495°, brown needles, is obtained ; its hyposulphite vat is deep blue and dyes cotton in the same shades, changing to orange in air.　　C. S.

[Preparation of a Bromo-derivative of 4-Chloro-1-methyl-anthraquinone.]—FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 259881).—When a boiling nitrobenzene solution of 4-chloro-1-methylanthraquinone (15 parts) is treated with a similar solution of bromine (8·5 vols.) it furnishes a *compound* which separates in orange crystals as the solution cools; the m. p. is above 300°.

<div align="right">F. M. G. M.</div>

Preparation of Condensation Products in the Anthra-quinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 261737). —The *compound* (annexed formula) is obtained when 1 : 2-diaminoanthraquinone and an-thraquinone - 2 - aldehyde are heated together in pyridine solution at 120°; the aldehyde can be replaced in this reaction by ω-chloro- or ω-dichloro-methylanthraquinones, and the diamine by 2 : 3-diaminoanthraquinone.
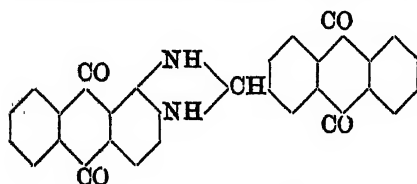
<div align="right">F. M. G. M.</div>

[Preparation of Anthraquinone Derivatives.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 262252).—4-a-*Anthra-quinonylaminoanthraquinone*-1 : 2-*acridone* is obtained by condensing 4-aminoanthraquinoneacridone with a-chloroanthraquinone in the presence of aluminium chloride, zinc chloride, or sulphuric acid.

<div align="right">F. M. G. M.</div>

Preparation of Condensation Products in the Anthracene Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 260662). —The removal of chlorine or bromine by means of potassium iodide and acetone has previously been described (A., 1911, i, 432), and it is now found that when ω-dibromo-2-methylanthraquinone is heated with potassium iodide (2 parts) and acetone (10 parts) at 100° during twelve to fourteen hours, it yields the previously-described compound, $C_{30}H_{14}O_4$ (A., 1908, i, 999).

When ωω'-tetrabromo-2 : 2'-dimethyl-1 : 1'-dianthraquinonyl (A., 1912, i, 361) is treated in a similar manner, it gives rise to a *di-phthaloylphenanthren*, an orange-brown powder; the preparation of other derivatives by this reaction is discussed.

<div align="right">F. M. G. M.</div>

Synthesis of the Higher Indandiones. II. MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1913, 399, 182—241).—The reaction whereby diethylmalonyl chloride and benzene or its homologues yield diethylindandiones (A., 1910, i, 490) has been examined in the cases where dimethylmalonyl chloride or dipropylmalonyl chloride is used.

[With MARGARETE DECKERT.]—Dimethylmalonyl chloride, which is identified in small quantities best by conversion into *dimethylmalon-anilide*, $CMe_2(CO \cdot NHPh)_2$, m. p. 202·5—203°, reacts abnormally with benzene in the presence of aluminium chloride, yielding ultimately phenyl *iso*propyl ketone and two *substances*, $C_{17}H_{16}O_2$, m. p. 193—194°

and 125° respectively, which are probably $\beta\beta$-dibenzoylpropane and the lactone of β-hydroxy-$\beta\beta$-diphenyl-$\alpha\alpha$-dimethylpropionic acid; the two substances have not been further examined on account of the difficulty of separating them.

Dimethylmalonyl chloride condenses normally with other aromatic hydrocarbons, yielding substituted indandiones. Thus its reaction with *p*-cymene in carbon disulphide in the presence of aluminium chloride leads to the formation of 2 : 2 : 4-*trimethyl*-7-*isopropylindandione*,

$$C_6H_2MePr^{\beta}\underset{CO}{\overset{CO}{<}}>CMe_2,$$
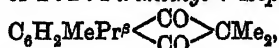
b. p. 168—169°/14 mm., D^{15} 1·634, which is oxidised to an *acid*, probably $C_6H_2(CO_2H)_2\underset{CO}{\overset{CO}{<}}>CMe_2$, m. p. 179—180°, by nitric acid at 115—140°.

Under conditions similar to the preceding, dimethylmalonyl chloride and naphthalene ultimately yield three *substances*, $C_{15}H_{12}O_2$, m. p. 101°, 121°, and 137° respectively, which can only be separated by the mechanical sorting of their well-defined crystals. The constitutions of the three substances have been determined by oxidising the products of their decomposition by alkalis. The substance, m. p. 101°, is 2 : 2-*dimethyl*-1 : 8-*naphthindandione*, $C_{10}H_6\underset{CO}{\overset{CO}{<}}>CMe_2$, since it is converted by boiling 50% potassium hydroxide into 1-*isobutyrylnaphthalene*-8-*carboxylic acid*, $CHMe_2\cdot CO\cdot C_{10}H_6\cdot CO_2H$, m. p. 158·5—159·5°, hexagonal plates and prisms, which is oxidised to naphthalic anhydride by nitric acid at 125°. The substance, m. p. 121°, is 2 : 2-*dimethyl*-1 : 2-*naphthindandione*, $C_{10}H_6\underset{CO}{\overset{CO}{<}}>CMe_2$; it is converted by 50% potassium hydroxide into 1(or 2)-*isobutyrylnaphthalene*-2(or 1)-*carboxylic acid*, m. p. 153—154°, which is oxidised to naphthalene-1 : 2-dicarboxylic acid and its anhydride by boiling glacial acetic acid and nitric acid, D 1·4. The third substance, m. p. 137°, must be 2 : 2-*dimethyl*-2 : 3-*naphthindandione* by exclusion; it is converted by alkali into 2-*isobutyrylnaphthalene*-3-*carboxylic acid*, m. p. 164—165·5°, which is oxidised to *naphthalene*-2 : 3-*dicarboxylic acid*, m. p. 241° (decomp.), by nitric acid at 120°, or by boiling nitric and glacial acetic acids. Naphthalene-2 : 3-dicarboxylic acid forms an anhydride, m. p. 245°, by heating, and yields a fluorescein by the usual method.

By direct treatment with nitric acid at 120—140°, 2 : 2-dimethyl-1 : 8-naphthindandione yields a *nitro*-derivative, $C_{15}H_{11}O_4N$, m. p. 162°, yellow needles; a *dinitro*-derivative, $C_{15}H_{10}O_6N_2$, m. p. 245—248° (decomp.), microscopic, hexagonal plates or prisms, and a colourless *acid*, m. p. 237—239° (decomp.); 2 : 2-dimethyl-1 : 2-naphthindandione yields a yellow *substance* containing nitrogen, and an *acid*, $C_{13}H_{10}O_6$, m. p. 229—233° (decomp.), which is probably 2 : 2-*dimethylindandione*-4 : 5-*dicarboxylic acid*, $CMe_2\underset{CO}{\overset{CO}{<}}>C_6H_2(CO_2H)_2$, whilst 2 : 2-dimethyl-2 : 3-naphthindandione yields nitrogenous products and a *substance*, m. p. 186—187° (decomp.), colourless needles.

When heated above their m. p.'s, 1-*iso*butyrylnaphthalene-8-carboxylic acid and 2-*iso*butyrylnaphthalene-3-carboxylic acid are converted

into *lactones*, $C_{10}H_6\begin{smallmatrix}CO\underline{\hspace{1em}}\\C(:CMe_2)\end{smallmatrix}\rangle O$, m. p. 117·5—118·5° and 174—175°
respectively, which are isomeric with the original indandiones; the
former lactone is re-converted into 1-*iso*butyrylnaphthalene-8-carboxylic
acid by boiling 50% potassium hydroxide, is oxidised to naphthalic
anhydride by boiling nitric and glacial acetic acids, and yields a *bromo*-
derivative, m. p. 141°, microscopic prisms, by bromination in chloro-
form. 1(or 2)-*iso*Butyrylnaphthalene-2(or 1)-carboxylic acid remains
unchanged by heating above its m. p.

Assuming that the $-CH_2 \cdot CH_2-$ group is unattacked, acenaphthene
could yield three indandiones by reaction with dimethylmalonyl chloride
and aluminium chloride in carbon disulphide. Actually only two are
obtained, having m. p. 127·5—129° and 176·5—177·5° respectively.
The former crystallises in colourless needles, and is 2 : 2-*dimethyl*-
3 : 4-*acenaphthindandione*, $CMe_2\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle C_{10}H_4\langle\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}$, since it is con-
verted by boiling 50% potassium hydroxide into 3-iso*butyrylacenaph*-
thene-4-carboxylic acid, $\begin{smallmatrix}CO_2H\underline{\hspace{1em}}\\CHMe_2 \cdot CO\end{smallmatrix}\rangle C_{10}H_4\langle\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}$, m. p. 176° (decomp.),
colourless, microscopic plates, which is oxidised to naphthalene-
1 : 4 : 5 : 8-tetracarboxylic acid by alkaline potassium permanganate.
The isomeride, m. p. 176·5—177·5°, crystallises in pale yellow needles,
and is named *dimethylisoacenaphthindandione* ; its formula has not
been definitely determined.

The oxidation of 2 : 2-dimethyl-3 : 4-acenaphthindandione by sodium
dichromate and boiling glacial acetic acid yields 2 : 2-*dimethyl*-1 : 8-
naphthindandione-4 : 5-*dicarboxylic acid*, $CMe_2\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle C_{10}H_4(CO_2H)_2$,
m. p. 208—209° (*anhydride*, m. p. 207—208°).

When heated above its m. p., 3-*iso*butyrylacenaphthene-4-carboxylic
acid is converted into a *lactone*, $\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}\rangle C_{10}H_4\begin{smallmatrix}CO\underline{\hspace{1em}}\\C(:CMe_2)\end{smallmatrix}\rangle O$, m. p.
175—176°, orange needles, which is oxidised by boiling acetic and
nitric acids to *acenaphthalic anhydride* (anhydride of *acenaphthene*-
3 : 4-*dicarboxylic acid*), $\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}\rangle C_{10}H_4\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle O$, m. p. 293—294°, pale
brown leaflets. *Acenaphthalic acid* forms an *ammonium* salt, m. p. 283°,
yields its anhydride by heating, does not form a fluorescein, and
dissolves in concentrated sulphuric acid, yielding a pale yellow solution
with a splendid sky-blue fluorescence.

The reaction between anthracene and an excess of dimethylmalonyl
chloride in the presence of aluminium chloride leads to the formation
of 2 : 2-*dimethylanthraceneindandione*, $C_6H_4\langle\begin{smallmatrix}CH\\CH\end{smallmatrix}\rangle C_6H_2\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle CMe_2$,
m. p. 148·5—149·5°, brownish-red needles or plates, which is oxidised
by chromic and acetic acids to 2 : 2-*dimethylanthraquinoneindandione*,
$C_6H_4\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle C_6H_2\langle\begin{smallmatrix}CO\\CO\end{smallmatrix}\rangle CMe_2$, m. p. 231—232°, pale yellow prisms,
and is converted by boiling 50% potassium hydroxide into an *isobutyryl*-

anthracene-o-carboxylic acid, $C_6H_4 \!\!<^{CH}_{CH}\!\!> C_6H_2(CO_2H)\cdot COPr^\beta$, m. p. 203—205°, dark brown prisms; the latter, heated above its m. p., is converted into a *lactone,* $C_6H_4 \!\!<^{CH}_{CH}\!\!> C_6H_2 \!\!<^{CO-----}_{C(:CMe_2)}\!\!> O$, m. p. 141—142·5°.

Dimethylmalonyl chloride and phenanthrene in carbon disulphide in the presence of aluminium chloride yield ultimately a *dimethylphenanthreneindandione,* m. p. 207—208°, pale yellow needles, which is converted into *dimethylphenanthraquinoneindandione,* $C_{19}H_{12}O_4$, m. p. 246—247°, orange needles, by oxidation, and into a mixture of two isomeric acids by concentrated potassium hydroxide.

[With MAX ROTHSCHILD.]—Dipropylmalonyl chloride is characterised by conversion into the *dianilide,* $CPr_2^\cdot(CO\cdot NHPh)_2$, m. p. 168—168·5°, colourless prisms, and the *bisphenylhydrazide,* $C_{21}H_{28}O_2N_4$, m. p. 216—217°; by warming with carbonyl chloride in toluene at 100°, the latter is converted into the *diazolone,* $^{CO---O}_{NPh\cdot N}\!\!> C\cdot CPr_2^\cdot\cdot C \!\!<^{O-CO}_{N\cdot NPh}$, m. p. 157—158·5°.

Dipropylmalonyl chloride condenses normally with benzene or other aromatic hydrocarbons in the presence of aluminium chloride. Thus benzene yields, in addition to a small quantity of δδ-*dibenzoylheptane,* m. p. 106—107°, 2 : 2-*dipropylindandione,* $C_6H_4 \!\!<^{CO}_{CO}\!\!> CPr_2^\cdot$, b. p. 168—172°/14 mm., D 1·0390, which is converted into phthalic acid by oxidation. *p*-Cymene yields 4-*methyl*-2 : 2-*dipropyl*-7-*isopropylindandione,* $C_6H_2MePr^\beta \!\!<^{CO}_{CO}\!\!> CPr_2^\cdot$, m. p. 94·5°, colourless needles. Diphenyl yields a *phenyldipropylindandione,* $C_{21}H_{22}O_2$, m. p. 221·5°, colourless needles, the constitution of which has not been definitely determined. Naphthalene does not yield definite condensation products, but acenaphthene yields two *isomerides,* m. p. 154—154·5° and 126° respectively. The former crystallises in yellow needles, and is converted by boiling concentrated aqueous alkalis, or, better, by sodium and boiling alcohol into α-*propylvalerylacenaphthenecarboxylic acid,* $^{CH_2}_{CH_2}\!\!> C_{10}H_4(CO_2H)\cdot CO\cdot CHPr_2^\cdot$, m. p. 166—167°, yellowish-brown leaflets. The isomeride, m. p. 126°, crystallises in yellow leaflets, and does not yield definite products by decomposition by alkalis.

Dipropylmalonyl chloride yields oily or amorphous products with anthracene, phenanthrene, and retene, but condenses with thiophen in the presence of aluminium chloride and carbon disulphide to form ultimately *dithiophenoyldipropylmethane,* $CPr_2^\cdot(CO\cdot C_4SH_3)_2$ or $CPr_2 \!\!<^{C(C_4SH_3)_2}_{CO}\!\!> O$, m. p. 192·5°, yellow needles, and *thiophenoyldipropylmethane,* $C_{12}H_{18}OS$, b. p. 158—163°/25 mm.
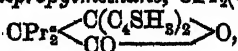
A table is given of the colours of the fluorescent solutions of the preceding substances in concentrated sulphuric acid.   C. S.

Action of Nitrogen Trioxide on Camphene. Nitrocamphene and Dinitrohydroxycamphane. PETER LIPP (*Annalen*, 1913, **399**, 241—260).—By the oxidation of *iso*camphane by nitric acid the author obtained (A., 1911, i, 731), amongst other products, a substance, $C_{10}H_{15}O_2N$, m. p. 64°, which is identical with so-called camphenile nitrite obtained by Jagelki by the action of nitrogen trioxide on camphene. The author's opinion that the substance is a nitro-compound (*loc. cit.*) has now been confirmed. He has, therefore, re-examined the action of nitrogen trioxide on camphene.

l-Camphene in petroleum (b. p. 30—40°) at −16° is treated with nitrogen trioxide (from arsenious oxide and nitric acid, not from sodium nitrite), whereby a faintly olive-green oil is produced, which decomposes at the ordinary temperature. The solvent is removed and the oily residue, after distillation with steam, is treated with aqueous potassium hydroxide. The deep red alkaline solution is treated as described below, whilst the residue is the desired substance, l-*nitro-camphene* (annexed formula), m. p. 84—85°
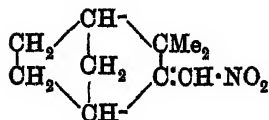
(corr.), $[\alpha]_D^{20} - 146\cdot4°$ in 20% benzene solution, which only differs from *dl*-nitrocamphene, m. p. 64°, in its m. p. and optical activity. The evidence for the presence of a nitro-group is the following: (i) The faintly yellow colour of the substance may be due to the presence of the nitro-group in the neighbourhood of the double linking. (ii) By treatment with alcoholic ammonia at 110—120°, the substance is converted into *l*-camphenilone and nitromethane (identified in the form of methylamine); by the action of boiling, aqueous alcoholic potassium hydroxide, the substance yields *l*-camphenilone and potassium nitroacetate. The nitro-group, therefore, is attached directly to a carbon atom. (iii) By reduction in ethereal solution by aluminium amalgam and water, the substance is converted into, not only ammonia and camphenilanaldehyde (which are the products of reduction in acid or in alkaline solution), but also into *camphenilanaldoxime*,

$$C_8H_{14}:CH\cdot CH:N\cdot OH,$$
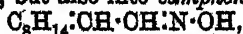
b. p. 134—135°/12 mm., a colourless, viscous liquid (*hydrochloride*,

$$C_{10}H_{18}ONCl,$$
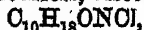
m. p. 90—92°, white, crystalline powder). The formation of camphenil-analdoxime is quite analogous to the production of aldoximes by the reduction of nitro-olefines in neutral solution. (iv) The conversion of nitrocamphene into tricyclenic acid by concentrated sulphuric acid is to be described fully in a future communication. The first product is a *sulphate* of camphenylhydroxamic acid, $C_{10}H_{15}O_5NS$, decomp. 127°; this is decomposed by warm water into sulphuric acid and *camphenyl-hydroxamic acid*, $C_{10}H_{17}O_3N$, decomp. 163°. The latter is decomposed by sulphuric acid into hydroxylamine and camphenylic acid, and from the latter, by loss of water, tricyclenic acid is produced. The whole change is analogous to the conversion of a primary nitro-compound into a carboxylic acid containing the same number of carbon atoms.

A second product of the action of nitrogen trioxide on camphene is the oily substance, $C_{10}H_{16}O_8N_2$, described by Jagelki as camphene

nitrosite. However, the substance, the *potassium* salt, $C_{10}H_{15}O_4N_2K$, garnet prisms or bronze leaflets, decomp. 207—209°, of which is contained in the deep red alkaline solution mentioned above, is, when pure, crystalline, m. p. 158·5° (corr.), and has the formula $C_{10}H_{16}O_5N_2$.

The substance is regarded as *ωω-dinitro-2-hydroxycamphane*,

$$CH(NO_2)_2 \cdot C \underset{CH(OH) \cdot CH_2}{\overset{CH_2---CH_2}{<}} \overset{}{>} CH,$$
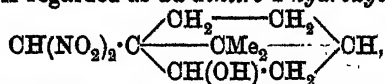
for the following reasons: The presence of the hydroxyl group is shown by the formation of an *acetyl* derivative, $C_{12}H_{18}O_6N_2$, m. p. 74—75° (corr.), stout plates. The substance, as a secondary alcohol, is oxidised to ketopinic acid by alkaline potassium permanganate at 50—60°. The presence of a *gem*-dinitro-group is suggested by the intense red colour of the potassium salt and by its reconversion into the colourless parent substance by carbon dioxide, and is confirmed by the reduction of an ethereal solution of the substance by aluminium amalgam and water, whereby hydroxylamine and an *oxime*, $C_{10}H_{17}O_2N$, m. p. 127—128·5°, colourless needles, are produced; the oxime is probably 2-*hydroxycamphan-ω-aldoxime*, $C_8H_{15}O \cdot C \cdot CH \cdot NOH$, but the aldehyde obtained from it has not been thoroughly examined owing to lack of material.

The formation of a camphane derivative, ωω-dinitro-2-hydroxy-camphane, from camphene by the action of nitrogen trioxide is effected possibly by the intermediate production of nitrocamphene. This view, however, is not altogether supported by the fact that nitrocamphene and nitric acid, D 1·514, after being kept for four days yield a substance which dissolves in alkalis with a deep red colour, but cannot be isolated, the chief product of the reaction being ketopinic acid, (p-*bromophenylhydrazone*, $C_{16}H_{19}O_2N_2Br$, m. p. 165—166° (corr.), straw-yellow leaflets). Possibly the nitrocamphene and the nitrous acid in the nitric acid form a nitrolic acid, the camphene ring changing at the same time to the camphane ring; the nitrolic acid is then oxidised to ketopinic acid. Attempts to unite nitrocamphene and nitrous acid directly have been unsuccessful. C. S.

Action of Methyl Iodide and Magnesium on Menthone. ALEXANDER E. ARBUZOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 700).— The author claims priority for Zelinsky (A., 1901, i, 660) and himself (A., 1908, i, 555) over Vanin (A., 1912, i, 788). T. H. P.

Oil of Adansonia Grandidieri. VICTOR THOMAS and F. BOIRY (*Bull. Soc. chim.*, 1913, [iv], **13**, 827—832).—On extraction with ether, the entire seeds of *Adansonia Grandidieri* yield 43% of oil, whilst the decorticated seeds give 64·5%. The oil obtained from the former has m. p. 20—21°; temperature of solidification, 13°; D^{20} 0·9190; n^{40} 1·4585; saponification number, 192·4; iodine number, 65·4—66·1; Reichert-Meissl number, 0·77; Hehner number, 95·5, whilst that obtained from the latter has m. p. 39—40°; temperature of solidification, 33°; D^{40} 0·9135; n^{40} 1·4521; saponification number, 196; iodine number, 36·9. After removal of the fatty acids, the oils from the entire (i) and decorticated seeds (ii) have the following constants:

m. p. (i) 51—52°; (ii) 45—46°; temperature of solidification, (i) 44·5°; acid number, (i) 179; (ii) 204·5; saponification number, (i) 202·5; (ii) 207·6; iodine number, (i) 66·3—66·9; (ii) 34·5—35; iodine number after acetylation, (i) 25·7; (ii) 26·8.

The oil consists of a mixture of esters of solid and unsaturated liquid acids in the proportion of 42% of the former and 58% of the latter. It is further characterised by the presence of a considerable quantity of a lactone, the precise nature of which has not been determined owing to lack of material. It has an iodine number 67·2, and when treated with bromine yields a liquid bromo-derivative.

The mixture of acids contains myristic acid, 7·6%; palmitic acid, 32·5%; oleic acid, 36·5%; linoleic acid, 8·7%, and lactone, 11·41%.

H. W.

Essential Oils. V. Essence of Cypress. GUSTAVE LALOUE (*Bull. Soc. chim.*, 1913, [iv], 13, 752—754. Compare A., 1911, i, 138; 1912, i, 574, 636).—The author has studied the oils obtained from the branches of *Cupressus sempervirens fastigiata*, L., and *Cupressus lusitanica*, Mill. The latter species yields rather more oil than the former. The oil from the former is brownish, and has D^{15} 0·8744; $a_D +12°6'$; acid number, 0·7; saponification number, 4·9; it dissolves in 3·5 vols. of alcohol (90%). The acetylated oil has $a_D +14°16'$; saponification number, 14·7. The oil from the latter is yellow. Its constants are D^{15} 0·8723; $a_D +9°10'$; soluble in 3 vols. of 90% alcohol; acid number, 1·05; saponification number, 9·8; saponification number after acetylation, 26·6; a_D of acetylated oil, $+8°36'$.

Practically no oil could be extracted from the seeds of *C. sempervirens*. The strobiles, freed from seeds, yielded 0·415% of an amber-coloured oil, D^{15} 0·8739; $a_D +29°52'$; soluble in 4 vols. of 90% alcohol; acid number, 1·0; saponification number, 9·8; saponification number after acetylation, 21·0; a_D of acetylated oil, $+29°48'$. H. W.

Components of the Essence of Seseli bocconi. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 116—121. Compare A., 1912, i, 123).—In addition to *l*-pinene and β-phellandrene, previously recorded, this oil contains a dicyclic aldehyde, a second carbonyl compound accompanying the aldehyde, a dicyclic primary alcohol, an unsaturated secondary alcohol, and *d-a*-methylbutyric, formic and acetic acids.

Oxidation of the primary alcohol with potassium dichromate and sulphuric acid yields an aldehyde, the *semicarbazone* of which,

$$C_{11}H_{19}ON_3,$$

has m. p. 148—158°. This aldehyde appears to be identical with that of the essential oil mentioned above, so that the aldehyde of the oil probably has the formula $C_{10}H_{16}O$, and the alcohol the composition $C_{10}H_{18}O$. R. V. S.

New Biochemical Syntheses of Glucosides of Alcohols. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], 8, 109—112).—Positive results indicating the formation of β-glucosides have been obtained with the following alcohols. In all cases 100 c.c.

of acetone, containing 20 grams of water per 100 grams of acetone, and 2 grams of dextrose were used, and varying quantities of alcohol and emulsin added. The isolation and characterisation of the glucosides has not yet been effected. The alcohols used were octyl, hexadecyl, benzaldehydecyanohydrin, *cyclo*hexanol, 2-methyl*cyclo*hexanol, α-naphthyl, borneol, morphine, also *tert.*-amyl alcohol and ethylphenylglycollyl ether.

Evidence is also quoted for the synthesis of α-glycerolglucoside. The action of dried yeast on a solution containing 4 grams of salicin and 5 grams of dextrose per 100 c.c. caused an increased dextrorotation. This is considered to indicate the attachment of the alcoholic hydroxyl in salicin to dextrose in the α-position. E. F. A.

Biochemical Synthesis of Glucosides of Multivalent Alcohols: α-Glucosides of Glycerol and Glycol. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1913, **157**, 405—408). —α-Glucosidase is capable of exerting a synthesising effect on solutions of glycerol and dextrose in water, the optimum effect being obtained with solutions containing 60 grams of glycerol in 100 c.c. The product is hydrolysed on the addition of water and maceration with more of the α-glucosidase (compare Bayliss, this vol., i, 919). Mixtures of glycol and dextrose are similarly synthesised, the reaction being more rapid than with glycerol. W. G.

Cymarin, the Active Principle of Apocynum cannabinum and Apocynum androsœmifolium. E. IMPENS (*Pflüger's Archiv,* 1913, **153**, 239—275).—Finnemore (P., 1909, **25**, 77) obtained as the active principle of the roots and rhizomes of *A. cannabinum,* "cynotoxin," whilst Moore (T., 1909, **95**, 734) prepared from *A. androsœmifolium,* "apocynamarin." It is now shown that these plants really contain the same bitter principle, *cymarin,* which is so susceptible to the influence even of weak organic acids that the two substances mentioned above may well be decomposition products. Taub and Fickewirth have isolated it by extracting the drug with carbon tetrachloride, dissolving the extract with alcohol, precipitating resins by means of warm water, clarifying the filtrate with basic lead acetate, and, after removing the lead and concentrating under reduced pressure, extracting the residue with chloroform. The cymarin was then precipitated by light petroleum and recrystallised from methyl alcohol. It forms colourless, glistening prisms, m. p. 135—140°, $C = 63.6\%$, $H = 8.4\%$. It is not a glucoside. A series of pharmacological experiments is described which shows that it corresponds in activity with digitalis, being slightly more potent as a diuretic and slightly less so as a cardiac stimulant. J. C. W.

Action of Alkyloxides on Hæmin and its Derivatives. I. Simplification of Hæmin by Potassium Alkoxides and a New Formation of Mesoporphyrin. HANS FISCHER and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1913, **87**, 38—50).—On heating hæmin in an autoclave with potassium methoxide at 220° a considerable quantity of phyllopyrrole is obtained, together with a little trimethylpyrrolepropionic acid.

With potassium ethoxide a mixture of the two dimethyldiethyl-pyrroles is formed :

I. NH$\diagdown\begin{smallmatrix}\text{CMe:CMe}\\\text{CEt=CEt}\end{smallmatrix}$,   II. NH$\diagdown\begin{smallmatrix}\text{CMe:CEt}\\\text{CEt=CMe}\end{smallmatrix}$
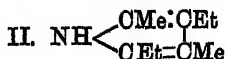
in which (I) predominates.

The reaction with alkyloxides is accordingly similar to the reduction effected by hydrogen iodide in the α-position; alkylation follows the simplification of the molecule by reduction.

The hæmin complex remains intact when it is heated with sodium methoxide at 200°. On treatment of the reaction product with hydrogen bromide in acetic acid, the iron is eliminated and meso-porphyrin obtained.   E. F. A.

The Difference between the Hæmocyanins according to their Zoological Origin. CHARLES DHÉRÉ (*Compt. rend.*, 1913, **157**, 309—312).—The preliminary results of an investigation into the differences in composition, constitution, and properties of hæmo-cyanins derived from the blood of different classes of invertebrates. The specimens examined were precipitated more or less completely on dialysis, the oxyhæmocyanin from the snail being obtained in a crystalline form, whilst the others were all amorphous. The behaviour was also varied on applying the biuret test for copper by addition of aqueous sodium hydroxide. Variations were found in the colour of solutions of different samples in N/10-acetic acid, but they all exhibited similar ultra-violet absorption spectra.   W. G.

Studies on Melanin. V. A Comparison of Certain Nitrogen Ratios in Black and in White Wool from the Same Animal. ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1913, **35**, 1262—1268. Compare A., 1910, i, 760; 1911, ii, 908; 1912, i, 290). —In order to determine if possible whether the chromogen utilised in the formation of melanin is part of the normal structure of keratin or whether it is secreted solely for pigment formation, the author has made comparative analyses of black and white wool from the same animal. No definite conclusion can be drawn, although the evidence seems somewhat in favour of the latter view.

The distribution of nitrogen in the two wools is very similar, with the exception that the presence of the pigment in black wool causes an excess of 3·54% in the humin nitrogen with a corresponding deficiency of 2·50% in the amino-nitrogen in the filtrate from the bases. The total nitrogen content of the white wool was 16·27%, whilst that of the black wool was 15·11%.   D. F. T.

[**Carminic Acid.**]   OTTO DIMROTH (*Annalen*, 1913, **399**, 378).— The author has received information that cochineal, contrary to his recent statement (this vol., i, 977), has been used in dyeing cotton.
                                                                           C. S.

Green Animal Colouring Matters. HANS PRZIBRAM (*Pflüger's Archiv*, 1913, **153**, 385—400).—The green colouring matters in *Bacillus Rossii*, *Dixippus morosus*, grasshoppers, locusts, Egyptian

praying-crickets, the Spanish fly, the skin of frogs, *Bonellia viridis*, and the leaves of the sea-lettuce, fir, syringa, maize, and blackberry have been compared. Ethereal or sometimes alcoholic extracts of equal colour intensity were heated for some time with saturated alcoholic potassium hydroxide, treated with a few drops of concentrated sulphuric or nitric acid, and also examined in the spectroscope. Many authors have doubted that the pigment in these animals is essentially different from chlorophyll, but the present investigations confirm the author in his view that animals develop a different colouring matter. Only in the case of the plant-eating insects could there be any suspicion, from the spectroscopic examination, that a little genuine plant chlorophyll was also present in the extract. In the flesh-eating insects, even in the wing cases of the praying-cricket, there is a different pigment, "animal green." The sea-worm, *Bonellia viridis*, contains a pigment of its own, "bonellein."

The author reviews the literature on the absorption spectra of chlorophyll and animal colouring matters, and finally tabulates the following characteristics. I. Chlorophyll.—Becomes turbid and precipitates black, flocculent masses on heating with alcoholic potassium hydroxide for some time; is only slightly bleached by strong acids, and shows a strong absorption band between 544 and 537 $\mu\mu$. II. Animal green.—Deposits coloured masses and clarifies with alcoholic potassium hydroxide; almost bleached by fuming nitric acid; rendered turbid and brown by sulphuric acid; shows no distinct band between 544 and 537 $\mu\mu$, and no shadow near 630 $\mu\mu$. III. Bonellein.—Coloured violet or blue by strong acids; shows a number of weak bands, and a strong one between 651 and 623 $\mu\mu$.   J. C. W.

Azomethine Dyes from β-Furylacraldehyde. WILHELM KÖNIG (*J. pr. Chem.*, 1913, [ii], **88**, 193—226).—In the presence of perchloric and hydrobromic acids, β-furylacraldehyde readily reacts with primary aromatic amines and with secondary amines of the tetrahydroquinoline and dihydroindole series in alcoholic solution, yielding blue dyes, related to the furfuraldehyde dyes already described by the author (A., 1906, i, 109) and having the following constitution (X = Br or ClO₄):

(I.) NRR'·CH:CH·CH:C(OH)·CH:CH·CH:NRR'X.

The dyes give violet-blue or greenish-blue alcoholic solutions, which rapidly lose their colour when kept. This disappearance of the blue colour is due to the removal of one of the amine residues and the formation of furfuraldehyde derivatives of the formula :

(II.) $\begin{matrix} \text{CH·CH} \\ \| \quad\quad \\ \text{CH——O} \end{matrix}$ >C·CH:CH·CH:NRR'X.
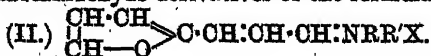
The latter compounds have been isolated in the form of their perchlorates, (i) by heating the perchlorates of the blue dyes, derived from cyclic secondary amines, in glacial acetic acid solution, and (ii) by the direct interaction of molecular amounts of the amines and β-furylacraldehyde in an alcoholic solution of perchloric acid.

That these compounds have the above constitution (II) and not the open-chain formula, NRR'·CH:CH·CH:C(OH)·CH:CH·CHO, has been

established (i) by the action of phenylhydrazine, which results in the removal of the amino-group and the formation of β-furylacraldehyde-phenylhydrazone (V below), and (ii) by the great similarity in the absorption spectra of the perchlorates of the condensation products, formed by cinnamaldehyde and β-furylacraldehyde with 6-methoxy-tetrahydroquinoline (thalline); the condensation product from cinnamaldehyde undoubtedly has the constitution represented in formula III, and hence the analogous product from β-furylacraldehyde must be represented by a similar formula (IV).

$$(\text{III.}) \quad CH_2 {<}^{C_6H_3(OMe)}_{CH_2-CH_2} {>}N{<}^{ClO_4}_{CH\cdot CH:CHPh}$$

$$(\text{IV.}) \quad CH_2 {<}^{C_6H_3(OMe)}_{CH_2-CH_2} {>}N{<}^{ClO_4}_{CH\cdot CH:CH\cdot C}{-}^{CH\cdot CH}_{O}{>}CH.$$
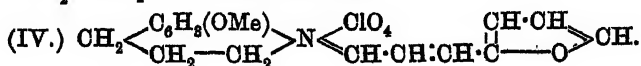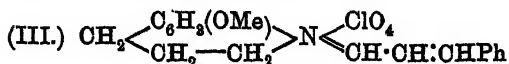
The author discusses both the mechanism of the formation of the dyes and also the relationship between their absorptive power and constitution from the point of view of Kauffmann's theory of partial valency, and, using Gebhard's method of representing the distribution of the partial valencies, assigns to the dyes the following constitution :
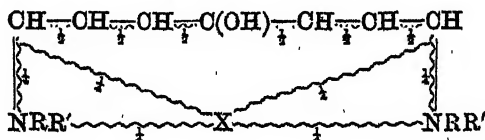
$$CH{\cdot\cdot}CH{\cdot\cdot}CH{\cdot\cdot}C(OH){\cdot\cdot}CH{\cdot\cdot}CH{\cdot\cdot}CH$$

NRR'⸺⸺⸺⸺X⸺⸺⸺⸺NRR'

β-Furylacraldehydephenylhydrazone,

$$C_4H_3O\cdot CH:CH\cdot CH:N\cdot NHPh \text{ (V)},$$

prepared from its components in alcoholic solution, is precipitated from the latter solution in citron-yellow needles, which are transformed by crystallisation from light petroleum into colourless crystals, m. p. 132°.

β-Furylacraldehyde condenses with m-nitroaniline in boiling alcoholic solution, yielding the *anil*, $C_4H_3O\cdot CH:CH\cdot CH:N\cdot C_6H_4\cdot NO_2$. This forms citron-yellow needles, m. p. 105°, and yields a *perchlorate*, which crystallises in orange prisms, and is converted by contact with primary or secondary aromatic amines into blue dyes.

The dyes described below were all prepared by the addition of the requisite amine (2 mols.) to a well cooled solution of β-furylacraldehyde (1 mol.) in a small quantity of alcohol, containing either hydrogen bromide (1 mol.) or perchloric acid (1 mol.). They all crystallise with $1H_2O$.

The *bromide* of the dye from the aniline (formula I, R = H, R' = Ph, X = Br) crystallises in dark bluish-green, microscopic needles, m. p. about 102°; the *perchlorate* in blue needles, m. p. 90°.

The *perchlorate* of the dye from m-toluidine forms blue needles, m. p. 108°; that from p-anisidine has m. p. about 115°.

The *bromide* of the dye from methylaniline (I, R = Me, R' = Ph) has m. p. 103°, and on treatment with aniline is converted into the

corresponding dye derived from aniline ; the perchlorate forms lustrous, blue needles, m. p. 110°.

Tetrahydroquinoline yields a dye which forms a *bromide*, m. p. about 125°,

$$\begin{matrix} CH_2 \cdot C_6H_4 \\ CH_2-CH_2 \end{matrix} > N \cdot CH:CH \cdot CH:C(OH) \cdot CH:CH \cdot CH:NBr < \begin{matrix} C_6H_4 \cdot CH_2 \\ CH_2-CH_2 \end{matrix},$$
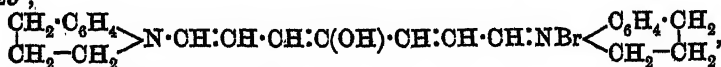
and a *perchlorate*, m. p. 118°.

The *perchlorates* of the dyes from 6-methyl- and 5-methyl-tetrahydroquinolines have m. p. 132° and 126° respectively.

The dye from 6-methoxytetrahydroquinoline forms a *bromide*, m. p. 129°, and a *perchlorate*, m. p. 121°.

2-Methyldihydroindole yields a dye, of which the *bromide* has m. p. 138°, and the *perchlorate*, m. p. 131°.

The *bromide* of the dye from a-methylphenomorpholine,

$$\begin{matrix} O-\!\!-C_6H_4 \\ CH_2 \cdot CHMe \end{matrix} > N \cdot CH:CH \cdot CH:C(OH) \cdot CH:CH \cdot CH:NBr < \begin{matrix} C_6H_4-O \\ CHMe \cdot CH_2 \end{matrix},$$
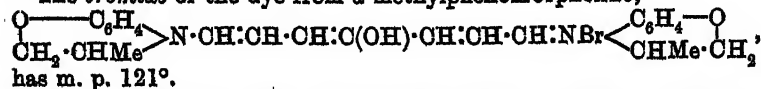
has m. p. 121°.

When heated in acetic acid solution the perchlorate of the dye from methylaniline yields the *compound*,

$$C_4H_3O \cdot CH:CH \cdot CH:NMePh \cdot ClO_4,$$
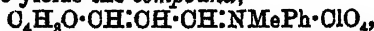
which forms citron-yellow crystals, m. p. 176°, and is transformed into the original perchlorate on treatment with methylaniline.

In a similar manner the perchlorate of the dye from 6-methyltetrahydroquinoline yields the *compound*

$$C_4H_3O \cdot CH:CH \cdot CH:N(ClO_4) < \begin{matrix} C_6H_3Me \\ CH_2 \cdot CH_2 \end{matrix} > CH_2.$$
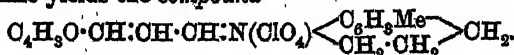
On crystallisation from glacial acetic acid this separates in long red and yellow needles, m. p. 204°, which have the same composition and cannot be separated by crystallisation from solvents ; the yellow modification passes into the red form on continued heating at 140—150°.

The *perchlorate* of the condensation product from 6-methoxytetrahydroquinoline and β-furylacraldehyde (formula IV), prepared by mixing the components in molecular proportions in alcoholic solution, forms red crystals, m. p. 188°, resembling chromium trioxide.

The corresponding *perchlorate* from cinnamaldehyde (III) forms orange crystals, m. p. 204° ; the *bromide* crystallises in long, orange-red needles, m. p. 185°, containing $1H_2O$.

By the interaction of furfuraldehyde and *m*-nitroaniline in alcoholic solution, Schiff (A., 1880, 391) obtained a substance, which he considered to have the formula : $C_4H_3O \cdot CH(OH) \cdot NH \cdot C_6H_4 \cdot NO_2$. The author finds, however, that the substance is not a furfuraldehyde derivative, but a pyrrole derivative of the following

constitution : $CH < \begin{matrix} CH-\!\!-CH \\ N(C_6H_4 \cdot NO_2) \end{matrix} > C \cdot CH:N \cdot C_6H_4 \cdot NO_2$. It separates

from ethyl alcohol in orange-yellow crystals, containing the solvent (1 mol.), m. p. 167—168°, and forms a *perchlorate*,

$$C_{17}H_{12}O_4N_4, HClO_4, C_2H_6O,$$
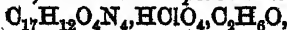
which crystallises in microscopic, brownish-red needles, m. p. 173° (decomp.).

Details of the methods employed in the spectrographic examination of the compounds described in the paper are also given. F. B.

Derivatives of Tetronic Acid. LUDWIG WOLFF (*Annalen*, 1913, **399**, 309—316).—[With H. JUNKER.]—*Bistetronic acid*,

$$\overset{CH_2 \cdot C(OH)}{\underset{O \longrightarrow CO}{}} > C \cdot C < \overset{C(OH) \cdot CH_2}{\underset{CO \longrightarrow O}{}},$$
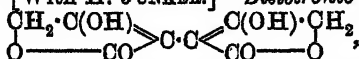
m. p. 235°, colourless, crystalline powder, is obtained by heating *ethyl dibromodiacetylsuccinate* (prepared by the bromination of ethyl diacetyl-succinate in chloroform) at 150—160°, or by treating a boiling aqueous solution of bromotetronic acid with propylidenebistetronic acid and sodium carbonate and subsequently acidifying the solution. Bistetronic acid and ferric chloride develop a blue coloration in aqueous solution and a green in alcohol. The *anilide*, $C_{14}H_{11}O_5N$, m. p. 216°, crystallises in leaflets, and the *dibenzoyl* derivative, $C_{22}H_{14}O_8$, m. p. 215°, in needles.

[With W. HEROLD.]—In general, a-alkyltetronic acids are converted by nitrogen trioxide into nitroso-compounds, $O < \overset{CH_2 \cdot CO}{\underset{CO \longrightarrow CR \cdot NO}{}}$, in the absence of water, and into oximes, $CO_2H \cdot CH_2 \cdot O \cdot CO \cdot CR:NOH$, in the presence of water; in the latter case, when the alkyl group R contains more than one carbon atom, it is eliminated in the form of an aldehyde and a-oximinotetronic acid is obtained. Thus 2-ethyltetronic acid and hot aqueous sodium nitrite, in the presence of a little hydrochloric acid, yield acetaldehyde, a-oximinotetronic acid, and *a'-oximinobutyryl-glycollic acid*, $CO_2H \cdot CH_2 \cdot O \cdot CO \cdot CEt:NOH$, m. p. 171°, colourless needles. In a similar manner, 2-benzyltetronic acid yields benzaldehyde, 2-oximinotetronic acid, and *a'-oximino-β'-phenylpropionylglycollic acid*, $CO_2H \cdot CH_2 \cdot O \cdot CO \cdot C(:NOH) \cdot CH_2Ph$, m. p. 146°, which dissolves in concentrated nitric acid with a blue colour, and is converted into a-oximino-β-phenylpropionic acid by hot aqueous sodium hydroxide, and into the corresponding *amide*, $C_9H_{10}O_2N_2$, m. p. 147°, needles, by aqueous ammonia.

By treatment with 100% nitric acid at 0°, 2-methyltetronic acid or 2-nitroso-2-methyltetronic acid is converted into a neutral *substance*, $C_5H_5O_6N$, m. p. 68°, colourless plates, which probably has the formula
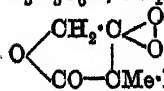
$$O < \overset{CH_2 \cdot C}{\underset{CO \longrightarrow CMe \cdot NO_2}{}} < \overset{O}{\underset{O}{}} .$$ It does not react with ferric chloride or respond to Liebermann's nitroso-reaction, exhibits powerful oxidising properties, and is decomposed by boiling water into dimethyl diketone, hydrogen cyanide, carbon dioxide, and nitric acid. In a similar manner, 2-nitroso-2-ethyltetronic acid is converted into a *substance*, $C_6H_7O_6N$, m. p. 43°, colourless needles. C. S.

Structural Formula of the Polymeride of the Anhydride of Anethole Glycol. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 93—94. Compare A., 1908, i, 901).—The author now assigns to this polymeride a formula of the type

$$R \cdot C_9H_2Me < \overset{O}{\underset{O}{}} > C_9H_2Me \cdot R.$$
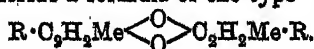
R. V. S.

Reactions of the Formamidines. III. Synthesis of *iso*-Oxazolone, *iso*Oxazole, Cyanoacetic and Benzoylacetic Acid Derivatives. FRANK BURNETT DAINS and E. L. GRIFFIN (*J. Amer. Chem. Soc.*, 1913, **35**, 959—970).—In extension of the earlier work (compare A., 1902, i, 602; A., 1909, i, 781) it is found that the methylene group of the *iso*oxazolones of the general formula $\begin{smallmatrix} CH_2 \cdot CO \\ | \quad\quad > O \\ CR = N \end{smallmatrix}$, like that of phenylmethylpyrazolone is capable of reacting with the arylformamidines.

Diphenylformamidine reacts with an equimolecular quantity of phenyl*iso*oxazolone at 120°, yielding aniline and 3-*phenyl-4-anilino-methylene-5-isooxazolone*, $\begin{smallmatrix} O-CO \\ \quad\quad > C:CH \cdot NHPh \\ N:CPh \end{smallmatrix}$, yellow, rhombic crystals, m. p. 145°; in a similar manner, di-*o*-tolylformamidine gives 3-*phenyl-4-o-toluidinomethylene-5-isooxazolone*, yellow crystals, m. p. 170°; 3-*phenyl-4-m-toluidinomethylene-5-isooxazolone*, yellow crystals, m. p. 158°; 3-*phenyl-4-p-toluidinomethylene-5-isooxazolone*, slightly red crystals, m. p. 190°; 3-*phenyl-4-o-anisidinomethylene-5-isooxazolone*, yellow needles, m. p. 138°; 3-*phenyl-4-p-anisidinomethylene-5-isooxazolone*, m. p. 168°; 3-*phenyl-4-p-phenetidinomethylene-5-isooxazolone*, m. p. 174°; 3 - *phenyl-4-ψ-cumidinomethylene-5-isooxazolone*, yellow needles, m. p. 180°; 3-*phenyl-4-m-nitroanilinomethylene-5*-isooxazolone yellow needles, m. p. 206°, and 3-*phenyl-4-p-bromoanilinomethylene-5-isooxazolone*, a pale yellow substance, m. p. 198°, are all obtainable similarly by applying the suitably substituted formamidine. The last-named product can also be obtained by the action of bromine on an acetic acid solution of phenylanilinomethylene*iso*oxazolone, when an intermediate red mono*bromo-compound*, m. p. 148°, is produced, which undergoes rearrangement in solution in pyridine or alcohol with formation of the phenylbromoanilinomethylene*iso*oxazolone.

No derivatives could be obtained from 3-methyl*iso*oxazolone by heating with formamidines as the temperature necessary to induce interaction caused decomposition of the products. Benzylidenemethyl-*iso*oxazolone, however, if heated with an equimolecular proportion of diphenylformamidine at 115—120°, yielded a mixture of benzylidene-aniline with 4-*anilinomethylene-3-methyl-5-isooxazolone*, pale yellow crystals, m. p. 158°, which dissolves unchanged in cold dilute alkalis, but with a warm solution of potassium hydroxide undergoes decomposition with deposition of aniline and needles of a potassium salt, decomp. 265—270°, of an unidentified *substance*; the above condensation product also reacts with bromine in acetic acid solution with precipitation of a yellow *substance*, which loses hydrogen bromide on drying, and when dissolved in alcohol or boiled with water or pyridine undergoes rearrangement into p-*bromoanilinomethylenemethylisooxazolone*, yellow needles, m. p. 204°, also obtainable from benzylidene-methyl*iso*oxazolone and di-*p*-bromodiphenylformamidine. A similar rearrangement has been previously noted (A., 1902, i, 602), the substance m. p. 148° having been since recognised as ethyl α-cyano-β-*p*-bromoanilinoacrylate, $C_6H_4Br \cdot NH \cdot CH:C(CN) \cdot CO_2Et$, and the explanation of this change appears to be expressed by the following

series of equations: $CHR_2 \cdot CH \vdots NPh + Br_2 = CHR_2 \cdot CHBr \cdot NBrPh = CR_2 \vdots CH \cdot NBrPh + HBr \longrightarrow CR_2 \vdots CH \cdot NH \cdot C_6H_4Br$, in the first stage of which the tautomeric form of the anilinomethylene derivative is involved. Diphenylformamidine also combines with bromine, giving a yellow additive *product*, m. p. 262°, which on treatment with potassium hydroxide solution decomposes into *p*-bromoaniline, *p*-bromoformanilide, and aniline.

That the reaction between benzylidenemethyl*iso*oxazolone and formamidines is a general one is evidenced by the following compounds which were also prepared : 4-*o-toluidinomethylene-3-methyl-5-isooxazolone*, pale red needles, m. p. 206° ; 4-m-*toluidinomethylene-3-methyl-5-isooxazolone*, brownish-white needles, m. p. 168° ; 4-p-*toluidinomethylene-3-methyl-5-isooxazolone*, yellow needles, m. p. 204°, which is decomposed by an alcoholic solution of hydrogen chloride with formation of ammonium chloride and *p*-toluidine hydrochloride, and on treatment with bromine in acetic acid solution gives a yellow additive *product*, m. p. 161—163° ; this regenerates the original substance when acted on by alcohol or potassium hydroxide ; 4-p-*anisidinomethylene-3-methyl-5-isooxazolone*, yellow needles, m. p. 190° ; 4-p-*phenetidinomethylene-3-methyl-5-isooxazolone*, yellow needles, m. p. 169° ; 4-m-*xylidinomethylene-3-methyl-5-isooxazolone*, colourless crystals, m. p. 166° ; 4-o-*anisidinomethylene-3-methyl-5-isooxazolone*, yellow crystals, m. p. 169°.

p-*Methoxybenzylidenemethyl*isooxazolone, deep yellow crystals, m. p. 178°, was prepared by a similar method to the corresponding benzylidene compound, namely, by the action of anisaldehyde and hydrochloric acid on the reaction mixture obtained from ethyl acetoacetate and hydroxylamine hydrochloride in aqueous alcohol containing some pyridine. It reacts with the formamidines in a similar manner to the benzylidene derivative, and on heating with di-ψ-cumylformamidine gave 4-*ψ-cumidinomethylene-3-methyl-5-isooxazolone*, a yellow, crystalline substance, m. p. 192°, together with anisylidene-ψ-cumidine, colourless crystals, m. p. 71°.

When a suspension of benzoylanilinomethyleneacetanilide,

$$NHPh \cdot CH \vdots CBz \cdot CO \cdot NHPh,$$

in alcohol is warmed for several hours with rather more than an equimolecular proportion of hydroxylamine hydrochloride and pyridine, there is produced 5-*phenyl*isooxazole-4-carboxyanilide,

$$\begin{matrix} N \!=\! CH \\ O \cdot CPh \end{matrix} \!\!> \!\! C \cdot CO \cdot NHPh,$$
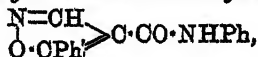
colourless needles, m. p. 135°, from the solutions of which in alkali acids precipitate benzoylcyanoacetanilide, $CN \cdot CHBz \cdot CO \cdot NHPh$, m. p. 203°. In a similar manner, 5-*phenyl*isooxazole-4-carboxy-o-*toluidide*, colourless needles, m. p. 114°, can be obtained from o-toluidino-methylenebenzoylaceto-o-toluidide, and by solution in alkali and reprecipitation by acid is converted into *benzoylcyanoaceto-o-toluidide*, colourless needles, m. p. 132° ; also 5-*phenyl*isooxazole-4-carboxy-p-*toluidide*, colourless needles, m. p. 158°, was prepared, which by successive treatment with alkali and acid yielded *benzoylcyanoaceto-p-toluidide*, colourless needles, m. p. 180° ; in the preparation of the

p-toluidinomethylenebenzoylaceto-*p*-toluidide required for the last synthesis, a quantity of *ethyl α-benzoyl-p-toluidinoacrylate*,

$$C_6H_4Me·NH·CH:CBz·CO_2Et,$$
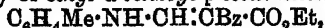
yellow flakes, m. p. 98°, was obtained. In an analogous manner, p-*anisidinomethylenebenzoylaceto-p-anisidide*, yellow crystals, m. p. 196°, obtainable by heating a mixture of ethyl benzoylacetate and di-*p*-anisylformamidine at 140°, could be converted into 5-*phenylisooxazole-4-carboxy-p-anisylamide*, colourless needles, m. p. 142°, which under the influence of alkali rearranges to *benzoylcyanoaceto-p-anisidide*, colourless needles, m. p. 194°.

Derivatives of 5-methyl*isooxazole*-4-carboxylic acid can be obtained by taking arylaminomethyleneacetoaceto-arylamides in place of the analogous derivatives of benzoylacetic acid in the immediately pre-ceding general synthetic reaction, and the products under the influence of alkali readily pass into the corresponding amides of cyanoacetoacetic acid; 5-*methylisooxazole-4-carboxy-o-toluidide*, colourless needles, m. p. 112°, is converted by alkali into *cyanoacetoaceto-o-toluidide*,

$$CN·CHAc·CO·NH·C_6H_4Me,$$
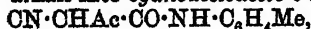
colourless needles, m. p. 110°; 5-*methylisooxazole-4-carboxy-p-toluidide*, colourless needles, m. p. 140°, is converted by alkali into *cyanoaceto-aceto-p-toluidide*, colourless needles, m. p. 176°. 5-*Methylisooxazole-4-carboxyanilide*, a colourless substance, m. p. 136°, which rearranges to cyanoacetoacetanilide, is difficult to isolate on account of its considerable solubility.

During the course of the investigation the following substances were also obtained apparently for the first time: *ethyl* m-*xylidino-methyleneacetoacetate*, $C_6H_3Me_2·NH·CH:CAc·CO_2Et$, colourless crystals, m. p. 122°, by heating ethyl acetoacetate with di-*m*-xylylformamidine at 120°; *cyanoaceto-m-toluidide*, colourless crystals, m. p. 138°, by heating together ethyl cyanoacetate and *m*-toluidine for several hours at 160°; *cyanoaceto-p-anisidide*, colourless crystals, m. p. 138°, by heating the two components at 160—170°.   D. F. T.

Oxindole and Thio-oxindole. CHARLES MARSCHALK (*J. pr. Chem.*, 1913, [ii], **88**, 227—250).—A recapitulation and extension of previous work (A., 1912, i, 303, 575).—Thionaphthenquinone reacts with hydrazine hydrate in boiling alcoholic solution, yielding a *substance* (probably a *hydrazone*), which crystallises in yellow leaflets, m. p. 128°, and when heated above its m. p. decomposes into nitrogen and thio-oxindole (2-keto-2 : 3-dihydro-1-thionaphthen). The latter com-pound is best prepared by heating o-thiolphenylacetic acid with phosphoric oxide in benzene solution. When prepared by this method and submitted to steam distillation, it is generally obtained in stout prisms, m. p. 44—45°, which on distillation under ordinary pressure are transformed into slender needles, m. p. 33—34°. The more fusible modification is also formed by distilling o-thiolphenylacetic acid alone, or heating it with acetic anhydride and distilling the product in steam. It differs from the modification of higher m. p. in giving at once a deep-blue coloration with ferric chloride. Only in one instance has it been found possible to transform the modification of m. p. 33—34° into the

less fusible variety, a specimen of the former substance, obtained by heating o-thiolphenylacetic acid with phosphoric oxide in benzene solution, being converted into the modification of higher m. p. by acidifying its solution in cold aqueous sodium hydroxide.

On treatment with nitrous acid, thio-oxindole yields thionaphthenquinone-3-oxime, m. p. 181° (Friedländer, A., 1908, i, 200, gives m. p. 186°). It couples with benzenediazonium chloride, yielding a substance, $C_{14}H_{10}ON_2S$, which crystallises in intensely red, lustrous needles, m. p. 159—160°, and is possibly identical with the phenylhydrazone of thionaphthenquinone (m. p. 165—166°) described by Friedländer (*loc. cit.*). With p-nitrobenzenediazonium chloride it forms a red *azo-dye*,

$$C_{14}H_9O_3N_3S,$$
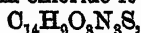
m. p. 271—272°.

The *azo-dyes* from a- and β-naphthalenediazonium chlorides crystallise in stout, brown needles, m. p. 192—193° and 154—156° respectively.

When heated with o-methoxybenzaldehyde in alcoholic solution in the presence of piperidine, thio-oxindole yields 2-*keto*-3-*o-methoxybenzylidene*-2 : 3-*dihydro*-1-*thionaphthen*,

$$OMe \cdot C_6H_4 \cdot CH:C \underset{C_6H_4}{\overset{CO}{<}} \!\!\! > S,$$
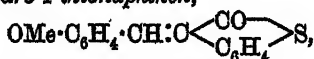
which forms yellow needles, m. p. 96—98°, and is hydrolysed by alcoholic potassium hydroxide to a-*thiolphenyl-o-methoxycinnamic acid*, $OMe \cdot C_6H_4 \cdot CH:C(C_6H_4 \cdot SH) \cdot CO_2H$, crystallising in stout, colourless needles, m. p. 134—136°.

It condenses with thionaphthenquinone-2-p-dimethylanil and acenaphthene in hot glacial acetic acid solution containing a little sulphuric acid, yielding 2 : 3'-bisoxythionaphthen (Friedländer, A., 1908, i, 673) and 8-oxy-6-oxythionaphthenylacenaphthene (Bezdzik and Friedländer, *loc. cit.*) respectively.

When heated with isatin in alcoholic solution, thio-oxindole forms an additive *compound*, $S \underset{CO}{\overset{C_6H_4}{<}} \!\!\! > CH \cdot C(OH) \underset{CO}{\overset{C_6H_4}{<}} \!\!\! > NH$, crystallising in colourless needles, which gradually become red at 135°, m. p. 155—160°. The additive compound gives a brown coloration with sulphuric acid, and when heated for a short time with glacial acetic acid containing a few drops of strong hydrochloric acid, is converted into 3'-*indoxyl*-3-*thionaphthen*-2'-*one*, $S \underset{CO}{\overset{C_6H_4}{<}} \!\!\! > C:C \underset{CO}{\overset{C_6H_4}{<}} \!\!\! > NH$, which crystallises in lustrous, silky, brown needles, m. p. 230°, and may also be obtained by the interaction of thio-oxindole or o-thiolphenylacetic acid and isatin in the presence of a mixture of glacial acetic and sulphuric acids (1 : 2) at the ordinary temperature.

(3')-5' : 7'-*Dichloroindoxyl*-3-*thionaphthen*-2'-*one*,

$$S \underset{CO}{\overset{C_6H_4}{<}} \!\!\! > C:C \underset{CO}{\overset{C_6H_2Cl_2}{<}} \!\!\! > NH,$$
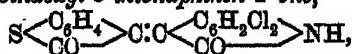
prepared by maintaining a solution of 5 : 7-dichloroisatin and thio-oxindole in the above acid mixture for three hours at the ordinary temperature, crystallises in dark brown needles, m. p. 330°.

The corresponding *dibromo*-derivative, from 5 : 7-dibromoisatin, forms brown needles, m. p. 331°. F. B.

The Anthraquinone Series. III. Anthraquinonethiazoles. FRITZ ULLMANN and WALTHER JUNGHANS (*Annalen*, 1913, **399**, 345—352).—*2-Phenyl-*4 : 5-(2' : 1')-*anthraquinonethiazole* (formula I), m. p. 291° (corr.), yellowish-green needles, is obtained by boiling 2-benzylideneamino-anthraquinone with sulphur and naphthalene, or, better, by heating 1-chloro-2-aminoanthra-quinone with potassium thiobenzoate and naphthalene at about 225°.
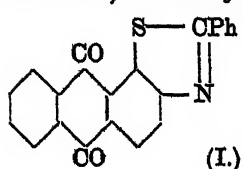
2-*Phenyl*-4 : 5-(1' : 2')-*anthraquinonethiazole* (formula II), m. p. 260° (corr.), brown needles, and 2-*phenyl*-4 : 5-(2' : 3')-*anthraquinonethiazole*, $C_6H_4\langle\begin{smallmatrix}CO\cdot C:CH\cdot C\cdot N\\CO\cdot C:CH\cdot C\cdot S\end{smallmatrix}\rangle OPh$, m. p. 336—337° (corr.), faintly yellow crystals, are prepared by the latter method from 2-bromo-1-aminoanthraquinone and 3-bromo-2-amino-anthraquinone respectively. The last-mentioned thiazole does not possess dyeing properties.

1 : 3 - Dibromo - 2 - aminoanthraquinone and potassium thiobenzoate react in boiling amyl alcohol, the initially-formed thiazole being converted into a *thiazole*-3 : 3'-*disulphide*, $C_{42}H_{20}O_4N_2S_4$, m. p. about 385°; by a similar method, 1-chloroanthraquinone is converted into the anthraquinonyl-1 : 1'-di-sulphide, m. p. 359°, obtained by Gattermann from anthraquinonyl-1-mercaptan.   C. S.

Selenodiarylamines. WILHELM CORNELIUS (*J. pr. Chem.*, 1913, [ii], **88**, 395—408).—The selenium analogues of thiodiphenylamine and its derivatives are readily obtained by heating diarylamines with selenium dichloride in benzene solution (compare Weizmann and Stephen, P., 1913, **29**, 196).

Selenodiphenylamine, $NH\langle\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}\rangle Se$, prepared from diphenylamine, crystallises in small, lustrous, yellow leaflets, m. p. 195°, which become greenish on exposure to air, owing to slight oxidation. Its constitution has been established by the formation of carbazole on distilling the substance with zinc dust or iron filings. With ferric chloride in alcoholic solution, it yields an emerald-green coloration. When heated with methyl iodide in methyl-alcoholic solution, it forms a *methyl* derivative, which crystallises in white needles, m. p. 138—139°, and is freed from the accompanying green oxidation product by reduc-tion with sulphurous acid in alkaline solution. The methyl derivative resembles the parent substance in yielding various characteristic colorations on treatment with oxidising agents. It forms a yellow *nitro*-compound, which is converted by reduction and subsequent oxidation with ferric chloride into a red dye.

When heated with acetic anhydride, selenodiphenylamine forms an *acetyl* derivative, crystallising in white flakes or stout, lustrous, prismatic crystals, m. p. 176°.

On treatment with concentrated nitric acid at 0°, it yields two isomeric *dinitroselenoxydiphenylamines*, $C_{12}H_7O_5N_3Se$, which are readily

separated by taking advantage of the insolubility of the α-isomeride in alcohol. The α-isomeride crystallises in clusters of small, light brown needles, melts with decomposition, and dissolves in aqueous alkalis and ammonia yielding strawberry-red solutions; the white *silver* and *mercuric* salts are mentioned. On reduction and subsequent oxidation, the α-compound gives rise to the selenium analogue of Lauth's violet, and, therefore must have the annexed constitution.
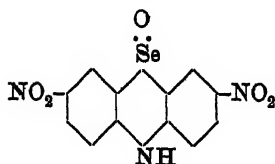
The β-isomeride forms a reddish-brown, crystalline mass, and is converted by successive reduction and oxidation into a reddish-violet *dye*. When treated with dilute nitric acid, selenodiphenylamine yields a *mononitro*-derivative, which, however, could not be separated from the accompanying dinitro-derivatives. On reducing the mixture of nitro-compounds with tin and hydrochloric acid, *aminoselenodiphenyl-amine*, $NH<\frac{C_6H_4}{C_6H_3(NH_2)}>Se$, separates in the form of its *stanni-chloride*. This crystallises in lustrous needles, and, on treatment with zinc and hydrochloric acid, yields the *zincichloride*, crystallising in small, broad, transparent needles. The free *base* is liberated from the latter compound by aqueous sodium hydroxide and crystallises in small, white, pearly, lustrous leaflets; the *hydrochloride* is precipitated in white needles by passing hydrogen chloride into a benzene solution of the base; the *acetyl* derivative has m. p. above 330° (decomp.).

Oxidation of the hydrochloride or zincichloride by means of ferric chloride in aqueous solution results in the formation of a dye, which is precipitated by the addition of sodium and zinc chlorides in the form of its *zincichloride*, $2\begin{vmatrix} N-C_6H_4 \\ NH\cdot C_6H_3 \end{vmatrix}>Se,H_2ZnCl_4$. This crystallises in very slender, bronze needles, dyes silk light blue to bluish-violet, and, on the addition of alkalis to its hot alcoholic solution, yields the free *base*, which forms a crystalline red powder, and is converted by hydrogen chloride in ether solution into the *hydrochloride*.

α-Dinitroselenoxydiphenylamine is reduced by stannous chloride and hydrochloric acid to *diaminoselenodiphenylamine stannichloride*,

$$2NH<\frac{C_6H_3(NH_2)}{C_6H_3(NH_2)}>Se,H_2SnCl_4,H_2O.$$
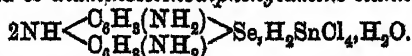
This crystallises in slender, lustrous, yellowish-brown needles, and is converted by the addition of zinc to its aqueous solution into the *zincichloride*, which is oxidised by ferric chloride to *selenonine*, the selenium analogue of Lauth's violet. The latter compound separates in the form of its *zincichloride*, $2\begin{vmatrix} N-C_6H_3(NH_2) \\ NH\cdot C_6H_3 \end{vmatrix}>Se,H_2ZnCl_4$, in very slender, felted, reddish-brown needles, having a bronze lustre. The dye *base*, obtained from the zincichloride by the action of aqueous sodium hydroxide, crystallises in small bronze needles and forms a *hydrochloride*, which crystallises in long, slender, felted needles, having a bronzy-green lustre, and dyes silk turquoise-blue.

The selenium analogue of methylene-blue has been prepared by the action of hydrogen selenide on p-nitrosodimethylaniline and subsequent oxidation of the resulting compound with ferric chloride in hydrochloric acid solution.

Selenophenyl-β-naphthylamine, $NH<^{C_6H_4}_{C_{10}H_6}>Se$, prepared by heating phenyl-β-naphthylamine with selenium dichloride in benzene solution, crystallises in small, yellow needles, m. p. 176°, and gives a greenish-blue coloration with sulphuric acid.

Seleno-α-dinaphthylamine, $NH<^{C_{10}H_6}_{C_{10}H_6}>Se$, from αα-dinaphthylamine, forms small, yellow needles, m. p. 176—177°.

Seleno-β-dinaphthylamine crystallises from benzene in slender, felted, yellowish-green needles, from nitrobenzene in long, pointed prisms, m. p. 245°, and from alcohol in tabular crystals. On treatment with nitric acid in acetic acid solution, it yields a yellow *nitro*-compound.

Seleno-p-ditolylamine crystallises in yellow, lustrous, broad scales, m. p. 240°. F. B.

New Derivatives of Artemisin and of Santonin. II. ENRICO RIMINI and TEMISTOCLE JONA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 28—32. Compare this vol., i, 748).—When artemisin is reduced with hydrogen in presence of palladium-black, *α-tetrahydroartemisin*, $C_{15}H_{22}O_4$, is obtained. It crystallises in plates, m. p. 192—193°, $[α]_D^{22} + 49.60°$ (in 2.671% alcoholic solution). From the mother-liquor a second hydro-derivative, *β-tetrahydroartemisin*, $C_{15}H_{22}O_4$, m. p. 165—167°, can be obtained. This substance has $[α]_D^{22} + 65.15°$ (in 2.670% alcoholic solution). Both tetrahydroartemisins are stable towards Baeyer's reagent. *α-Tetrahydroartemisinsemicarbazone*,
$$C_{15}H_{22}O_3:CH_3ON_3,$$
decomposes at 245°. *β-Tetrahydroartemisinsemicarbazone*,
$$C_{15}H_{22}O_3:CH_3ON_3,$$
decomposes at 257—258°. *α-Tetrahydroartemisinoxime*, $C_{15}H_{22}O_3:NOH$, decomposes at 248°. *β-Tetrahydroartemisinoxime*,
$$C_{15}H_{22}O_3:NOH,$$
decomposes at 242°. Artemisinoxime yields α-tetrahydroartemisin when hydrogenated in presence of palladium-black. When α-tetrahydroartemisin is dissolved in sodium hydroxide and the solution acidified with sulphuric acid at a low temperature, *α-tetrahydroartemisinic acid* can be extracted with chloroform; it softens and loses water at 55°, decomposing at 118°. Its *sodium* salt crystallises in needles. *β-Tetrahydroartemisinic acid* is similarly prepared, and is much more stable. It forms needles, m. p. 218—220° (decomp.), and on titration with alkali gives figures agreeing with the composition
$$C_{14}H_{23}O_3·CO_2H.$$
R. V. S.
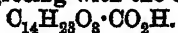
Action of the Halogens on Artemisin. ENRICO RIMINI and TEMISTOCLE JONA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 71—74. Compare preceding abstract).—When a solution of artemisin in glacial acetic acid is treated with a solution of hydrogen bromide and bromine in the same solvent, *artemisin dibromide hydrobromide*, $C_{30}H_{37}O_8Br_3$, is

obtained. This unstable oxonium compound, which readily loses bromine, forms lustrous, red crystals which decompose at 94°. Under slightly different experimental conditions, the compound described is accompanied by *monobromoartemisin*, $C_{15}H_{17}O_4Br$, a stable, yellow substance which becomes red at about 70° and decomposes at 95°.

Artemisin di-iodide hydriodide, $C_{30}H_{37}O_8I_3$, similarly prepared, is a brown, crystalline substance, m. p. 118—119° (decomp.).

By the action of chlorine on a chloroform solution of artemisin at 15°, a *chloroartemisin*, $C_{15}H_{15}O_8Cl_3$, is obtained, but the preparation is uncertain; the substance crystallises in needles, which decompose at 212°. When the chlorination is effected at 20°, a crystalline *chloroartemisin*, $|C_{15}H_{20}O_4Cl_2$, is obtained; it decomposes at 133°.

R. V. S.

Identity of Lycorine and Narcissine. YASUHIKO ASAHINA and Y. SUGII (*Arch. Pharm.*, 1913, **251**, 357—360).—The authors have examined the base lycorine, which together with a second base sekisanine was isolated by Morishima (A., 1899, i, 93) from the bulbs of *Lycoris radiata*. They are of opinion that lycorine, $C_{16}H_{17}O_4N$, m. p. 275° (decomp.), darkening at about 240°, $[\alpha]_D^{13}$ – 123·7° in alcohol and pyridine (*hydrochloride*, colourless needles, m. p. 217°; *picrate*, m. p. 195—202° [decomp.], yellow leaflets), is identical with the alkaloid narcissine, $C_{16}H_{17}O_4N$, m. p. 266—267°, $[\alpha]_D$ – 95·8°, colourless prisms (hydrochloride, m. p. 198—199°, colourless needles; picrate, m. p. 196—199°, yellow leaflets), obtained by Ewins (T., 1910, **97**, 2406) from the bulbs of *Narcissus pseudonarcissus*. C. S.

Formula of *apo*Morphine Hydrochloride. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 121—125).—Estimations of the water of crystallisation in *apo*morphine hydrochloride from various sources all indicate $\frac{3}{4}H_2O$. The amount of chlorine in the salt is that required by the formula $C_{17}H_{17}O_2N,HCl,\frac{3}{4}H_2O$, and the elementary analysis of *apo*morphine gives the composition $C_{17}H_{17}O_2N$. Dibenzoyl-*apo*morphine has, in freezing benzene, the composition required by the formula $C_{17}H_{15}N(OBz)_2$. R. V. S.

Preparation of Hydrogenised Alkaloids of the Morphine Group. HERMANN OLDENBERG and BABETTE OLDENBERG (D.R.-P. 260233).—Alkaloids of the morphine group are readily hydrogenised by the action of hydrogen in the presence of colloidal palladium, or a metal of the platinum group. *Hydromorphine*, $C_{17}H_{21}O_3N,H_2O$, fine needles, m. p. 155—157°, is obtained when morphine hydrochloride (10 parts) in 250 parts of water is shaken with a mixture of colloidal palladium (1 part) in 10 parts of water which has been saturated with hydrogen; the *hydrochloride* forms microscopic prisms; the *sulphate* is less readily obtained in crystalline form; it gives the colour reactions of Fröhde, Husemann, and Marquis.

Hydrocodeine, rhombic crystals, m. p. 62—63°, has also 1 mol. water of crystallisation and gives Fröhde's and Hesse's colour reactions.

Tetrahydrothebaine, $C_{19}H_{25}O_3N$, is prepared from thebaine and responds to Fröhde's and Erdmann's reagents; the *hydrochloride* forms

prisms; the *hydrogen tartrate* is obtained by the reduction of thebaine hydrogen tartrate.

The therapeutic action of these compounds is also discussed.

F. M. G. M

Berberine. II. Berberrubine. GEORG FRERICHS and P. STOEPEL (*Arch. Pharm.*, 1913, **251**, 321—339).—Berberrubine is best obtained by heating well dried berberine chloride at about 190° in a slow current of carbon dioxide. There can be little doubt that anhydrous berberrubine contains the annexed group. Since it is readily converted into berberine iodide by treatment with methyl iodide, other alkyl haloids may be expected to produce homologous berberines. Thus a large excess of ethyl iodide on the water-bath converts berberrubine into *ethylberberrubine iodide (homoberberine iodide)*, $C_{21}H_{20}O_4NI$, yellow or yellowish-brown needles, which reacts with boiling alcoholic $N/2$-potassium hydroxide and acetone to form *ethylberberrubineacetone*, $C_{24}H_{25}O_5N$, m. p. 159°, from which the salts of ethylberberrubine are obtained by heating with dilute acids; the *chloride*, $C_{21}H_{20}O_4NCl,2H_2O$, is described.
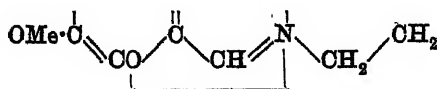
By boiling with dilute acetic and sulphuric acids and zinc and a little platinum, ethylberberrubine chloride is reduced and yields, after basification with aqueous ammonia, *ethyltetrahydroberberrubine*, $C_{21}H_{23}O_4N$, m. p. 129°, faintly yellow crystals, which resembles tetrahydroberberine throughout.

Berberrubine reacts additively, not only with alkyl haloids, but also with other organic halogen compounds. Ethyl bromoacetate and alcohol on the water-bath convert it into the *bromide* of *ethyl berberrubineacetate*, $C_{23}H_{22}O_6NBr$, yellow crystals, which is converted by digestion with silver oxide and hot water into *berberrubineacetic acid*, $C_{21}H_{17}O_6N,5H_2O$; a hot aqueous solution of the latter is converted into the *hydrochloride*, $C_{21}H_{17}O_6N,HCl,2H_2O$, yellow crystals, by N-hydrochloric acid.

In a similar manner, berberrubine and ethyl α-bromopropionate yield the *bromide* of *ethyl berberrubinepropionate*, $C_{24}H_{24}O_6NBr$, yellow needles, from which *berberrubinepropionic acid*, $C_{22}H_{19}O_6N,2H_2O$, yellow needles, is obtained; the *hydrochloride* of the latter also crystallises in yellow needles. Berberrubine does not react with ethyl β-iodopropionate.

Berberrubine, unlike berberine, is attacked by oxidising agents most readily in its methoxylated benzene nucleus. By treatment with hot 25% nitric acid it yields two crystalline substances, berberrubinone and berberrubinic acid, both of which are obtained in the form of nitrates. *Berberrubinone nitrate* (annexed formula) forms dark green, almost black, crystals, which are deep red by transmitted light, is converted into a *sulphate* (or mixture of normal and hydrogen sulphates), dark green crystals, by hot dilute sulphuric acid,
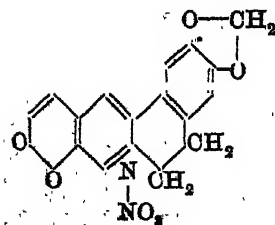
and by treatment with boiling dilute sulphuric acid and 30% sodium hydrogen sulphite is reduced to the sulphate of the corresponding quinol, *berberrubinol sulphate*, a yellow substance. From the hot solution of the latter, saturated sodium hydrogen carbonate liberates *berberrubinol*, $C_{18}H_{13}O_4N,3H_2O$, an amorphous, dark red powder.

Anhydrous berberrubinol is a phenol-betaine, and is therefore a completely demethylated berberine; it is not identical with Perkin's berberoline, which has the same composition.
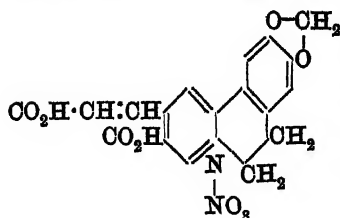
Berberrubinic acid nitrate (annexed formula) and the corresponding *chloride*, $C_{18}H_{14}O_6NCl$, form golden-yellow crystals, and are decomposed by water with the formation of *berberrubinic acid*, an amorphous, yellow substance, which is probably a betaine; it has not been obtained entirely free from the nitrate or chloride.

A hot aqueous solution of berberrubine is converted by sodium hypochlorite into *chloroberberrubine*, $C_{19}H_{14}O_4NCl$, reddish-brown needles, which forms a *chloride*, $C_{19}H_{15}O_4NCl_2,3H_2O$, orange-yellow crystals. Chloroberberrubine certainly contains the chlorine atom in the methoxylated benzene nucleus (probably in the meta-position to the methoxy-group), because by the prolonged action of sodium hypochlorite it is converted into the *lactam chloride*,

$$NCl\cdot CO—C\cdot CH\colon C\cdot O \diagdown CH_2,$$
$$CH_2\cdot CH_2\cdot C\cdot CH\colon C\cdot O \diagup$$
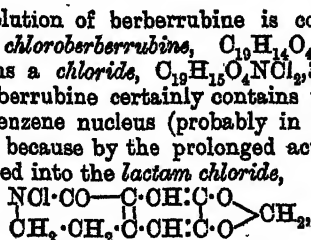
m. p. 114°, colourless needles, of ω-aminoethylpiperonylcarboxylic acid; the lactam-chloride, which can also be obtained by the action of sodium hypochlorite on berberine chloride or bromoberberrubine in hot aqueous solution, is converted into Perkin's lactam, m. p. 181°, by treatment with hot aqueous sodium sulphite.

Chloroberberrubine is reduced to *chlorotetrahydroberberrubine*, $C_{19}H_{18}O_4NCl$, m. p. 142°, colourless crystals (*hydrochloride*, white, crystalline powder), by zinc and platinum and hot dilute acetic and sulphuric acids, and reacts with methyl iodide at 100° to form *chloroberberine iodide*, $C_{20}H_{17}O_4NClI$; the latter, which resembles berberine iodide in its behaviour, reacts with alcoholic $N/2$-potassium hydroxide and acetone to form *chloroberberineacetone*, $C_{23}H_{22}O_5NCl$, m. p. 171°, yellow crystals. The following substances are obtained by methods similar to the preceding: *bromoberberrubine*, $C_{19}H_{14}O_4NBr$, reddish-brown needles, and its *chloride*, $C_{19}H_{15}O_4NClBr,3H_2O$, yellow crystals; *bromotetrahydroberberrubine*, $C_{19}H_{18}O_4NBr$, m. p. 145°, colourless crystals; *bromoberberine iodide*, $C_{20}H_{18}O_4NBrI$, golden-yellow leaflets, and *bromoberberine acetone*, $C_{23}H_{22}O_5NBr$, m. p. 153°, yellow crystals.

C. S.

Preparation of Hydrastinine from Berberine. EMMANUEL MERCK (D.R.-P. 259873. Compare VOSS, A., 1910, i, 415; Freund, A., 1912, i, 383, 487).—Phenyltetrahydroberberine (m. p. 222°) when digested with methyl iodide furnishes a *methiodide*, m. p. 243°.

Phenyldihydroberberine on electrolytic reduction gives rise to two

stereoisomeric phenyltetrahydroberberines with m. p.'s 222° and 202—204°; these can be separated by fractional crystallisation of their sulphates; the *methiodide* of the isomeride (m. p. 202—204°) has m. p. 247°.

When either of the foregoing phenyltetrahydroberberines is digested with silver chloride, and subsequently reduced with sodium amalgam, it yields a *base*, $C_{27}H_{29}O_4N$, m. p. 112—113° (the *hydriodide* has m. p. 218°), which on oxidation gives rise to hydrastinine.   F. M. G. M.

Reactions of the Formamidines. IV. FRANK BURNETT DAINS, O. O. MALLEIS, and J. T. MEYERS (*J. Amer. Chem. Soc.*, 1913, **35**, 970—976. Compare this vol., i, 1086).—The previous investigations have indicated that the general reaction of formamidines with compounds containing methylene hydrogen may be formulated :

$$CH_2XY + NR\!:\!CH\!\cdot\!NHR = CXY\!:\!CH\!\cdot\!NHR + NH_2R.$$
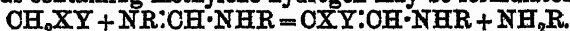
If Y is a carbethoxy-group the amine produced can react with it to give an amide and an alcohol. The occurrence of the second reaction is more marked the higher the temperature.

p-Aminophenylbenzyl ether (hydrochloride, m p. 222—223°; *benzoyl* derivative, m. p. 226—227°; *benzylidene* derivative, colourless leaflets, m. p. 118°; *anisylidene* derivative, m. p. 150°) when warmed with ethyl orthoformate readily enters into reaction, producing *di-p-benzyloxydiphenylformamidine*, $C_7H_7O\cdot C_6H_4N\!:\!CH\cdot NH\cdot C_6H_4\cdot OC_7H_7$, colourless crystals, m. p. 153°; *hydrochloride*, m. p. 261°; *picrate*, m. p. 209°. When heated with ethyl cyanoacetate at 120—130°, the formamidine reacts, producing aminophenylbenzyl ether and *ethyl α-cyano-β-p-benzyloxyanilinoacrylate*, $CH_2Ph\cdot O\cdot C_6H_4\cdot NH\cdot CH\!:\!C(CN)\cdot CO_2Et$, brown crystals, m. p. 120°. The formamidine reacts in the usual manner with ethyl malonate, giving *ethyl p-benzyloxyanilinomethylenemalonate-p-benzyloxyanilide*, colourless crystals, m. p. 131°, as with ethyl malonate the molecule of amine produced in the first stage of the reaction is always found to enter into amide formation. Ethyl acetoacetate with the formamidine yields products of both the first and second stages of the reaction, giving *ethyl p-benzyloxyanilinomethyleneacetoacetate*, $CH_2Ph\cdot O\cdot C_6H_4\cdot NH\cdot CH\!:\!OAc\cdot CO_2Et$, a pale yellow substance, m. p. 95°, together with *p*-benzyloxyanilinomethyleneacetoaceto-*p*-benzyloxyanilide, fine, yellow needles, m. p. 164°.

As was to be expected from experiments with other formamidines, phenylmethylpyrazolone readily reacts with di-*p*-benzyloxydiphenylformamidine, giving *1-phenyl-4-p-benzyloxyanilinomethylene-3-methyl-5-pyrazolone*, red needles, m. p. 181°.

When ethyl orthoformate is heated with *p*-aminodimethylaniline at 125° for two hours, *di-p-dimethylaminodiphenylformamidine*, m. p. 157°, is obtained, which gives a yellow *monohydrochloride*, m. p. 233°, a dihydrochloride and a colourless *trihydrochloride*, m. p. 193°; *picrate*, m. p. 172°. The formamidine reacts with ethyl malonate, yielding *ethyl p-dimethylaminoanilinomethylenemalonate-dimethylaminoanilide*, $NMe_2\cdot C_6H_4\cdot NH\cdot CH\!:\!C(CO_2Et)\cdot CO\cdot NH\cdot C_6H_4\cdot NMe_2$, m. p. 142°, and with ethyl cyanoacetate giving *ethyl α-cyano-β-p-dimethylaminoanilinoacrylate*, $NMe_2\cdot C_6H_4\cdot NH\cdot CH\!:\!C(CN)\cdot CO_2Et$, colourless needles, m. p. 134°. When heated with ethyl acetoacetate the amidine produced phenylene-

dimethyldiamine and *p-dimethylaminoanilinomethyleneacetoaceto-p-dimethylaminoanilide*, NMe$_2$·C$_6$H$_4$·NH·CH:CAc·CO·NH·C$_6$H$_4$·NMe$_2$, m. p. 178°, together with a little *ethyl dimethylaminoanilinomethyleneacetoacetate*, m. p. 88°.

Di-p-iododiphenylformamidine, C$_6$H$_4$I·N:CH·NH·C$_6$H$_4$I, colourless needles, m. p. 175°, is easily obtained by the combination of *p*-iodoaniline and ethyl orthoformate at water-bath temperature; *hydrochloride*, m. p. 249°; picrate, dark yellow crystals, m. p. 226°. With ethyl cyanoacetate at 125°, it produces *ethyl a-cyano-β-p-iodoanilinoacrylate*, brown needles, m. p. 154°, whilst with ethyl malonate *ethyl p-iodoanilinomethylenemalonate-p-iodoanilide*,

C$_6$H$_4$I·NH·CH:C(CO$_2$Et)·CO·NH·C$_6$H$_4$I,
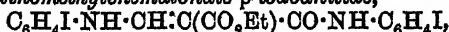
colourless crystals, m. p. 176°, is obtained. With ethyl acetoacetate the products are iodoaniline, *ethyl p-iodoanilinomethyleneacetoacetate,*, C$_6$H$_4$I·NH·CH:CAc·CO$_2$Et, colourless crystals, m. p. 96°, and *p-iodoanilinomethyleneacetoaceto-p-iodoanilide*, m. p. 184°. The formamidine also reacts with acetylacetone, producing *p-iodoanilinomethyleneacetylacetone*, CAc$_2$:CH·NH·C$_6$H$_4$I, pale yellow needles, m. p. 180°, whilst with benzylidenemethylisooxazolone at 140°, *3-methyl-4-p-iodoanilinomethylene-5-isooxazolone*,
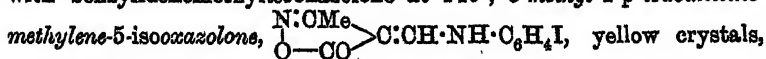
$\begin{smallmatrix} N:CMe \\ | \quad\quad \\ O—CO \end{smallmatrix}$ >C:CH·NH·C$_6$H$_4$I, yellow crystals,

m. p. 208°, is obtained. The *benzylidene* derivative, m. p. 85°, and *anisylidene* derivative, colourless needles, m. p. 151°, of *p*-iodoaniline were also prepared.

5-Iodo-*o*-toluidine (acetyl derivative, m. p. 176°, reacts quantitatively with bromine in chloroform solution producing 5-bromoaceto-*o*-toluidide, m. p. 158—159°; *benzylidene* derivative, colourless needles, m. p 55°) also reacts with ethyl orthoformate, giving *di-5-iododi-o-tolylformamidine*, C$_8$H$_8$MeI·N:CH·NH·C$_6$H$_3$MeI, needles, m. p. 169°; *hydrochloride*, m. p. 254°. This formamidine shows the usual behaviour towards compounds containing the methylene group, for example, with ethyl acetoacetate it forms *ethyl 5-iodo-o-toluidinomethyleneacetoacetate*, m. p. 137—138°, and *5-iodo-o-toluidinomethyleneacetoaceto-5-iodo-o-toluidide*, silky needles, m. p. 238°. With ethyl cyanoacetate and malonate the reaction products are *ethyl 5-iodo-a-cyano-o-toluidinoacrylate*, m. p. 207°, and *ethyl 5-iodo-o-toluidinomethylenemalonate-5-iodo-o-toluidide*, m. p. 201°. At 120° with benzylidenemethylisooxazolone the formamidine gives rise to *3-methyl-4-iodotoluidinomethylene-5-isooxazolone*, needles, m. p. 209°. D. F. T.

Preparation of Carbazolemonosulphonic Acids and their 9-Alkyl Derivatives. LEOPOLD CASSELLA & Co. (D.R.-P. 260898. Compare this vol., i, 516).—When carbazole (17 parts) is dissolved in 10—15 parts of hot nitrobenzene and cooled to 0° (when part of the carbazole separates), treated with chlorosulphonic acid (12 parts), and the temperature subsequently allowed to rise to 20°, it furnishes *carbazolesulphonic acid*, which is isolated in the form of its sodium salt, colourless, glistening leaflets; the *barium* salt, glistening scales, is more sparingly soluble. This compound condenses with *p*-nitrosophenol in concentrated sulphuric acid solution to furnish soluble blue dyes containing sulphur.

9-*Ethylcarbazolesulphonic acid* can also be prepared in quantitative yield by this method.   F. M. G. M.

[Preparation of 9-Ethylcarbazole-3:6-diphthaloylic Acid.]
LEOPOLD CASSELLA & Co. (D.R.-P. 261495. Compare A., 1911, i, 567).
—9-Ethylcarbazole reacts with phthalic anhydride and aluminium chloride in nitrobenzene solution, yielding 9-*ethylcarbazole*-3:6-*di-phthaloylic acid*,

$$CO_2H \cdot C_6H_4 \cdot CO \diagdown \diagup CO \cdot C_6H_4 \cdot CO_2H$$
NEt
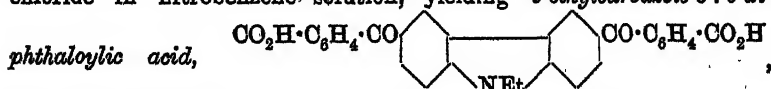
and this when heated with concentrated sulphuric acid at 100—105° during five hours gives rise to 2:3:6:7-*diphthaloyl-9-ethylcarbazole*,
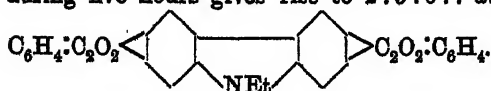
$$C_6H_4 \vdots C_2O_2 \diagup \diagdown C_2O_2 \vdots C_6H_4.$$
NEt

F. M. G. M.

Catalytic Decomposition of Acetonylacetonephenylhydr-azone. ALEXANDER E. ARBUZOV and N. E. CHRUCKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 699).—Catalytic decomposition of acetonylacetone-phenylhydrazone at 180—190° in presence of cuprous chloride yields ammonia, dimethylaminophenylpyrrole, benzene and aniline, the last two products probably arising from the decomposition of a little admixed phenylhydrazine.   T. H. P.

Catalytic Decomposition of Methyl Propyl Ketonephenyl-hydrazone. ALEXANDER E. ARBUZOV and A. P. FRIAUF (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 694—696).—Catalytic decomposition of methyl propyl ketonephenylhydrazone at 185—210° in presence of cuprous chloride yields, as principal product, *propylindole*, $C_{11}H_{13}N$, which is an almost odourless, pale yellow liquid, b. p. 155—156°/9 mm., and forms a *picrate*, $C_{17}H_{16}O_7N_4$, m. p. 148—149°. Small proportions of secondary gaseous and liquid products also result from the decomposition.   T. H. P.

Catalytic Decomposition of Dipropyl Ketonephenyl-hydrazone. ALEXANDER E. ARBUZOV and R. E. VAGNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 697—699).—Catalytic decomposition of dipropyl ketonephenylhydrazone at 175—235° in presence of cuprous chloride yields principally 3-*ethyl-2-propylindole*, $C_{13}H_{17}N$, which crystallises in unstable, colourless plates, m. p. 45·5°, and forms a *picrate*, $C_{13}H_{17}N, C_6H_3O_7N_3$, m. p. 117·5°. Other products, including aniline, are formed in small proportions.   T. H. P.

Syntheses in the Indole Group. V. Syntheses of *N*- and *C*-Substituted Derivatives of Scatole and Methylketole. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 190—211. Compare A., 1912, i, 649; this vol., i, 755).—3-Acetyl-2-methylindole can be obtained in 86% yield by the action of acetyl chloride on the magnesium derivative of 2-methylindole (*loc. cit.*). Its *hydrochloride*,
$$C_{11}H_{11}ON, HCl,$$

was also prepared. The *aurichloride*, $C_{11}H_{11}ON,HCl,AuCl_3$, becomes brown at about 135°, melting at 158° (decomp.). The *platinichloride*, $(C_{11}H_{11}ON,HCl)_2PtCl_4$, blackens above 170°, melting at 195° (decomp.). The hydrochloric acid solution of the ketone gives precipitates with phosphotungstic acid, potassium cadmium iodide, potassium bismuth iodide, and potassium dichromate.

1-*Acetylscatole*, $C_6H_4\!\!<\!\!\begin{smallmatrix}CMe\\NAc\end{smallmatrix}\!\!>\!\!CH$, is obtained by the action of acetyl chloride on the magnesium derivative of scatole, a low temperature being maintained with ice. It forms colourless needles, m. p. 68°, and has about the normal molecular weight in freezing benzene. Its constitution is shown by its yielding scatole when treated with alcoholic potassium hydroxide, and by the fact that it gives no precipitate with silver nitrate. In the preparation of 1-acetylscatole, a *substance* crystallising in needles of m. p. 146° is also obtained.

2-Acetylscatole is obtained when the above reaction is effected at the temperature of the water-bath. Its *hydrochloride* has the composition $(C_{11}H_{11}ON)_2,HCl$, and its solution gives precipitates with phosphotungstic acid, potassium bismuth iodide, potassium dichromate, and gold chloride. The *platinichloride* has the composition

$$(C_{11}H_{11}ON,HCl)_2PtCl_4,$$
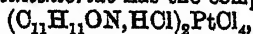
The action of propionyl chloride on the magnesium derivative of scatole yields both propionylmethylindoles, which can be separated by distillation with steam. 1-*Propionylscatole*, $C_{12}H_{13}ON$, has m. p. 45°. 2-*Propionylscatole*, $C_{12}H_{13}ON$, has m. p. 161°, and when fused with potassium hydroxide yields indole-3-carboxylic acid. 3-*Propionyl-2-methylindole*, $C_{12}H_{13}ON$, is obtained from propionyl chloride and the magnesium derivative of methylketole; it forms colourless crystals, m. p. 194°, and has about half the calculated molecular weight in freezing phenylhydrazine (K for phenylhydrazine is 58·59). Oxidation of the substance with potassium permanganate yields acetyl-*o*-aminobenzoic acid.

3-*Butyryl*-2-*methylindole*, $C_{13}H_{15}ON$, is prepared by the action of butyryl chloride on the magnesium derivative of methylketole; it is a white, crystalline substance, m. p. 157—158°, and tends to become yellow when exposed to the air.

3-Benzoyl-2-methylindole, $C_{16}H_{13}ON$ (from benzoyl chloride and the magnesium derivative of methylketole), forms colourless needles, m. p. 181°. When the reaction is effected at a low temperature, traces of a *substance* of m. p. 81° are produced, which is probably the 1-derivative.

R. V. S.

Condensation of Aldehydes with *N*-Mono-substituted *p*-Diamines. RICHARD SCHLÖGL (*J. pr. Chem.*, 1913, [ii], 88, 251—256).—An account of the preparation of a number of anils by the condensation of acetyl-*p*-phenylenediamine, *p*-amino-oxanilic acid, and *p*-aminophenylglycine with aromatic aldehydes.

The *salicylidene, cinnamylidene* (m. p. 120°), 3:4-*dihydroxybenzylidene, vanillidene*, and *furfurylidene* (m. p. 135°) derivatives of *p*-amino-

phenylglycine are prepared by warming the glycine with an alcoholic solution of the corresponding aldehyde.

The *benzylidene* derivative of *p*-aminophenyloxamic acid is obtained in the form of its *hydrochloride*, $C_{15}H_{12}O_3N_2Cl$, m. p. 180°, by heating an alcoholic suspension of the oxamic acid with benzaldehyde and hydrochloric acid.

The following compounds were prepared in a similar manner: the *hydrochlorides* of the *vanillidene* (m. p. 170°), *cinnamylidene* (m. p. 125°), and *furfurylidene* (m. p. 130°) derivatives of *p*-aminophenyl-oxamic acid, and the *hydrochlorides* of the *benzylidene* (m. p. 165°), *vanillidene* (m. p. 208°), and *cinnamylidene* (m. p. 195°) derivatives of acetyl-*p*-phenylenediamine.

The condensation *product* from acetaldehyde and *p*-aminophenyl-glycine forms a dark brown powder (decomp. 280°), insoluble in the ordinary solvents; attempts to effect a condensation of acetyl-*p*-phenylenediamine and *p*-aminophenylglycine with formaldehyde and acetaldehyde were unsuccessful.

All the derivatives mentioned above are readily resolved by boiling with water or alkali hydroxides into their components, and on account of the presence of the azomethine group, are coloured, those of *p*-aminophenylglycine being red.   F. B.

Hydrazones. LUIGI VECCHIOTTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 75—76).—Many nitrohydrazones exist in red and in yellow modifications. The present paper gives a list of these compounds and the forms observed in each instance.   R. V. S.

Extractives of Muscle. XIV. - Carnosine and Carnosine Nitrate. WLADIMIR GULEWITSCH (*Zeitsch. physiol. Chem.*, 1913, **87**, 1—11. Compare A., 1900, i, 516; 1905, i, 726; 1906, i, 627; 1907, i, 264, 436).—The purification of carnosine nitrate and carnosine is described. The nitrate crystallises in large, stellate aggregates of needles, m. p. 219° (decomp.), $[a]_D +23\cdot3°$ in 5% solution. The rotatory power increases slightly on dilution; it falls to about half its value in presence of nitric acid.

Carnosine crystallises in large, colourless needles, which unite to rosettes and cauliflower-like aggregates, m. p. 246—250° (decomp.). It has an insipid taste, and is strongly alkaline. It has $[a]_D +21°$, independently of the concentration. No racemisation takes place in preparing it from the nitrate.   E. F. A.

Preparation of Chloro- and Bromo-substitution Products of Indophenols and Indophenolic Substances or their Leuco-derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 260328 and 260329).—The action of *p*-nitrosophenol on carbazoles has previously been studied (A., 1906, i, 890; 1911, i, 1025), and halogen derivatives of these compounds have now been prepared.

When 4-dimethylamino-4'-hydroxydiphenylamine (230 parts) dissolved in concentrated hydrochloric acid (1700 parts) is treated at 10—15° with 150 parts of chlorine, it furnishes a *dichloro-4-dimethyl-amino-4'-hydroxydiphenylamine hydrochloride* in quantitative yield

which on oxidation gives rise to the corresponding *indophenol.* *Compounds* obtained by the action of chlorine on an *o*-dichlorobenzene solution of the following substances, and their oxidation products are described : from *p*-nitrosophenol with carbazole and the leuco-compound of the same; from *p*-nitrosophenol with *N*-methyl- or *N*-ethyl-carbazole and their leuco-compounds.
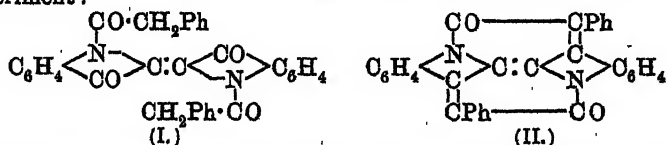
II. describes the preparation of the corresponding bromo-derivatives; in this case the reaction is carried out in *o*-dichlorobenzene solution.

F. M. G. M.

Constitution of Anilopyrine. Lino Metello Zampolli (*Boll. chim. farm.*, 1913, **52**, 502—504).—Polemical. A reply to Comanducci (this vol., i, 903). R. V. S.

Preparation of Red Condensation Products from Indigotin, its Homologues, and Substitution Products. Gesellschaft für Chemische Industrie in Basel (D.R.-P. 260243. Compare this vol., i, 763).—The action of phenylacetyl chloride on indigotin yields the red, crystalline *compounds* I or II, according to the conditions of the experiment :

$$C_6H_4\begin{array}{c}CO\cdot CH_2Ph\\<^{N}_{CO}>\end{array}C:C\begin{array}{c}<^{CO}_{N}>\\CH_2Ph\cdot CO\end{array}C_6H_4 \qquad C_6H_4\begin{array}{c}CO———CPh\\<^{N}_{C}>\end{array}C:C\begin{array}{c}<^{C}_{N}>\\CPh———CO\end{array}C_6H_4$$

(I.) (II.)

Analogous *compounds* prepared from tetrabromoindigotin are also described, which are of a somewhat bluer shade. F. M. G. M.

Benzoylation of Benziminazoles. Ludwig Wolff (*Annalen*, 1913, **399**, 297—309).—The reaction described by Bamberger and Berlé, in which secondary benziminazoles yield dibenzoyl-*o*-phenylene-diamine and a fatty acid by treatment with benzoyl chloride and aqueous sodium hydroxide, is explained by the author's experiments on the benzoylation of secondary or tertiary benziminazoles. He finds that secondary benziminazoles yield a benzoyl derivative. This benzoyl derivative or, in the case of a tertiary compound, the benzimin-azole itself forms an additive compound with benzoic acid, which probably has the constitution $C_6H_4\begin{array}{c}<^{NR\cdot COR'}_{NHBz}\end{array}$, and is decomposed by the alkali, yielding benzoylated *o*-phenylenediamines and a fatty acid.

[With R. Grün and F. Kolasius.]—The benziminazoles are treated with benzoyl chloride (2 or 4 mols.) and 10% sodium hydroxide (4 or 6 mols.). The precipitate is treated with ether, whereby the benzoyl derivative and oily products are dissolved; the residue is separated by chloroform into the acylphenylenediamine and dibenzoyl-*o*-phenylenedi-amine.

Benziminazole yields 1-benzoylbenziminazole (in very small amount), dibenzoyl-*o*-phenylenediamine, and *dibenzoylformyl-o-phenylene-diamine*, $NHBz\cdot C_6H_4\cdot NBz\cdot CHO$, m. p. 155—156°, needles, which is converted into formic acid and dibenzoyl-*o*-phenylenediamine by boiling

with alcohol, hydrochloric acid, or sodium hydroxide, and yields, by heating at 180—200°, carbon monoxide, benzoic acid, dibenzoyl-o-phenylenediamine, and 1-benzoylbenziminazole.

2-Methylbenziminazole yields 1-*benzoyl-2-methylbenziminazole*

$$C_6H_4 \left\langle \begin{matrix} NBz \\ N \end{matrix} \right\rangle CMe,$$
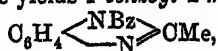
m. p. 86°, long needles, dibenzoyl-o-phenylenediamine, and *dibenzoyl-acetyl-o-phenylenediamine*, $NHBz \cdot C_6H_4 \cdot NBzAc$, m. p. 154°, prisms, which is converted into acetic acid and dibenzoyl-o-phenylenediamine by alcoholic hydrochloric acid or sodium hydroxide. 2-Ethylbenz-iminazole yields similar products; 1-*benzoyl-2-ethylbenziminazole*, colourless plates, has m. p. 82°, whilst *dibenzoylpropionyl-o-phenylene-diamine*, m. p. 124°, yields propionic acid and dibenzoyl-o-phenylene-diamine by treatment with sodium hydroxide or hydrochloric acid.

1-*Phenyl-2-ethylbenziminazole*, $C_6H_4 \left\langle \begin{matrix} NPh \\ N \end{matrix} \right\rangle CEt$, m. p. 45°, colour-less plates (*hydrochloride*, $C_{15}H_{14}N_2, HCl, H_2O$, prisms), is prepared by warming o-aminodiphenylamine with propionic anhydride and treating the resulting o-*propionylaminodiphenylamine*, $C_{15}H_{16}ON_2$, m. p. 144°, needles, with 10% hydrochloric acid; by treating the solution with sodium carbonate the benziminazole is precipitated. By the action of benzoyl chloride and 10% sodium hydroxide at 50°, it yields an oil and *propionyl-o-benzoylaminodiphenylamine*, $NHBz \cdot C_6H_4 \cdot NPh \cdot COEt$, m. p. 157°, plates, which is converted by warm alcoholic potassium hydroxide into propionic acid and o-benzoylaminodiphenylamine.

By treatment with benzoyl chloride and 10% sodium hydroxide at 50—60°, 1-phenyl-2-methylbenziminazole yields *acetyl-o-benzoylamino-diphenylamine*, $NHBz \cdot C_6H_4 \cdot NPhAc$, m. p. 122° (which is decomposed into acetic acid and o-benzoylaminodiphenylamine by hot alcoholic sodium hydroxide), a *substance*, $C_{28}H_{20}O_3N_2$, m. p. 165°, needles, and an oil which yields the substance, m. p. 165°, by further benzoylation.

The substance, m. p. 165°, is possibly $C_6H_4 \left\langle \begin{matrix} NPh \\ N \end{matrix} \right\rangle C \cdot CH : OPh \cdot OBz$,

since it does not develop a coloration with ferric chloride, and is con-verted in hot alcoholic solution, by elimination of a benzoyl group, into 1-*phenyl-2-phenacylbenziminazole*,

$$C_6H_4 \left\langle \begin{matrix} NPh \\ N \end{matrix} \right\rangle C \cdot CH_2 \cdot COPh,$$
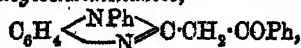
m. p. 119°, large plates or prisms. The latter develops a green coloration with ferric chloride, yields the substance, m. p. 165°, by benzoylation, and forms a *hydrochloride*, m. p. 240—245° (decomp.), *semicarbazone*, m. p. 202°, colourless prisms, and *phenylhydrazone*, m. p. 164°, colourless prisms.   C. S.

Pyrimidines. LXIII. A New Method of Synthesising Uramils and Thiouramils. TREAT B. JOHNSON and NORMAN A. SHEPHARD (*J. Amer. Chem. Soc.*, 1913, **35**, 994—1007).—Ethyl phthalimidomalonate reacts with thiocarbamide in warm alcoholic solution containing sodium ethoxide, the product being 2-thiouramil, $CS \left\langle \begin{matrix} NH \cdot CO \\ NH \cdot CO \end{matrix} \right\rangle CH \cdot NH_2$, which is probably formed by the hydrolysis of a previous condensation product; thiouramil when warmed with

sodium hydroxide solution undergoes hydrolysis, giving a substance, possibly *aminothiomalonuric acid*, $NH_2 \cdot CS \cdot NH \cdot CO \cdot CH(NH_2) \cdot CO_2H$.

Ethyl β-phthaliminoethylmalonate also condenses with thiocarbamide in the presence of sodium ethoxide in hot alcoholic solution, forming 2-*thio*-5-β-*phthaliminoethylbarbituric acid*,
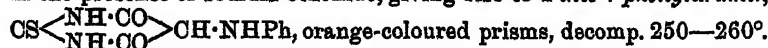
$$CS \overset{NH \cdot CO}{\underset{NH \cdot CO}{<}} > CH \cdot CH_2 \cdot CH_2 \cdot N \overset{CO}{\underset{CO}{<}} > C_6H_4,$$
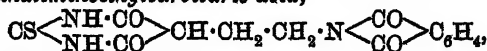
prisms, decomp. 265—270° (*sodium* salt, bright yellow), which on hydrolysis yields 2-*thio*-5-β-*aminoethylbarbituric acid*,

$$CS \overset{NH \cdot CO}{\underset{NH \cdot CO}{<}} > CH \cdot CH_2 \cdot CH_2 \cdot NH_2,$$
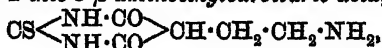
prisms, decomp. 298—300°, together with phthalic acid. If the condensation is effected with carbamide in place of thiocarbamide, phthalimide and 2 : 4 : 6-triketo-5-β-hydroxyethylpyrimidine (5-hydroxy-ethylbarbituric acid), $CO \overset{NH \cdot CO}{\underset{NH \cdot CO}{<}} > CH \cdot CH_2 \cdot CH_2 \cdot OH$, a pale yellow powder which did not melt below 300°, were obtained.

Ethyl anilinomalonate also readily reacts with thiocarbamide in the presence of sodium ethoxide, giving rise to 2-*thio*-7-*phenyluramil*, $CS \overset{NH \cdot CO}{\underset{NH \cdot CO}{<}} > CH \cdot NHPh$, orange-coloured prisms, decomp. 250—260°. With carbamide, however, a new type of compound was obtained, namely, *anilinomalonuric acid*, $NH_2 \cdot CO \cdot NH \cdot CO \cdot CH(NHPh) \cdot CO_2H$, prismatic crystals, which do not melt below 300°. This substance when digested with acetic acid undergoes dehydration to γ-*phenyluramil*, $CO \overset{NH \cdot CO}{\underset{NH \cdot CO}{<}} > CH \cdot NHPh$, an insoluble, crystalline powder. Allyl-thiocarbamide resembles thiocarbamide in behaving normally with ethyl anilinomalonate, and gives 2-*thio*-7-*phenyl*-1-*allyluramil*,

$$CO \overset{CH(NHPh) \cdot CO}{\underset{NH \underline{\hspace{1.5em}} CS}{<}} > N \cdot CH_2 \cdot CH : CH_2,$$
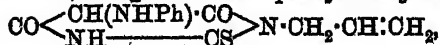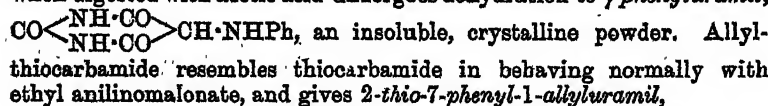
an insoluble powder, m. p. 185—187° (decomp.); *sodium* salt, brown powder.

When ethyl anilinomalonate is added to an alcoholic solution of sodium ethoxide, it gives a sodium derivative, which on the further addition of *p*-nitrobenzyl chloride reacts with the formation of two substances, one of which is insoluble in ether; the insoluble substance, needles or prisms, m. p. 180—182°, is probably 2-*p*-*nitrobenzylindoxyl*, $C_6H_4 \overset{CO}{\underset{NH}{<}} > CH \cdot CH_2 \cdot C_6H_4 \cdot NO_2$, whilst the soluble substance is *ethyl p*-*nitrobenzylanilinomalonate*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot C(NHPh)(CO_2Et)_2$, an oil, which on hydrolysis yields p-*nitrobenzylanilinomalonic acid*, prisms or leaflets, m. p. 205—210° (decomp.).　　　　　D. F. T.
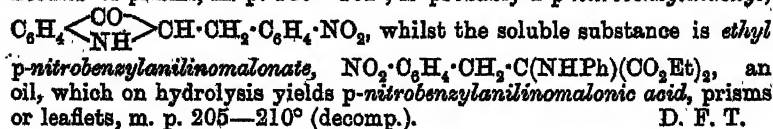
Pyrimidines. LXIV. Synthesis of 4-Methyl-5-ethyl-cytosine. TREAT B. JOHNSON and GEORGE C. BAILEY (*J. Amer. Chem. Soc.*, 1913, **35**, 1007—1014).—The paper commences with a summary of the alkyl derivatives of cytosine, $NH \overset{CO \underline{\hspace{1em}} N}{\underset{CH : CH}{<}} > C \cdot NH_2$, which have been prepared in the same laboratory.

When warmed together in sodium ethoxide solution, ethyl ethyl-acetoacetate and thiocarbamide react normally, giving the colourless

sodium salt of 2-*thio-4-methyl-5-ethyl*-1 : 2 : 3 : 6-*tetrahydro-6-pyrimidone*, $CS \diagdown_{NH \cdot CMe}^{NH-CO} \diagup OEt$, the free substance forming colourless prisms, m. p. 212°; alkylation is effected when the alcoholic solution of the sodium salt is treated with an alkyl haloid, for example, benzyl chloride gives rise to 2-*benzylthiol-4-methyl-5-ethyl*-1 : 6-*dihydro-6-pyrimidone*, blocks, m. p. 160°, whilst ethyl bromide yields 2-*ethylthiol-4-methyl-5-ethyl*-1 : 6-*dihydro-6-pyrimidone*, colourless crystals, m. p. 138°. The last-named derivative is converted by a molecular proportion of phosphorus pentachloride at 100° into 6-*chloro-2-ethylthiol-4-methyl-5-ethylpyrimidine*, b. p. 177—180°/21—23 mm., which is stable in contact with water, but is decomposed by warm alcohol, and also reacts with strong alcoholic ammonia at 140—150°, yielding 6-*amino-2-ethylthiol-4-methyl-5-ethylpyrimidine*, $CEt \diagdown_{CMe---N}^{C(NH_2):N} \diagup C \cdot SEt$, stout blocks, m. p. 89—91°. Both the benzylthiol- and the ethylthiol-substituted pyrimidines described above are converted by hydrolysis with acids into 4-methyl-5-ethyluracil, $CO \diagdown_{NH \cdot CMe}^{NH-CO} \diagup CEt$, the yield being quantitative when the ethylthiol compound is heated with a boiling aqueous solution of chloroacetic acid. The same uracil derivative is obtained in the action of chloroacetic acid on the parent substance, 2-thio-4-methyl-5-ethyl-1 : 2 : 3 : 6-tetrahydro-6-pyrimidone.

2-Ethylthiol-4-methyl-5-ethyl-1 : 6-dihydro-6-pyrimidone, when heated with aniline at 100° and with alcoholic ammonia at 150—160°, eliminates the thiol group with formation respectively of 2-*anilino-4-methyl-5-ethyl* 1 : 6-*dihydro-6-pyrimidone*, $CNHPh \diagdown_{N-CMe}^{NH \cdot CO} \diagup CEt$, m. p. 195°, and 2-*amino-4-methyl-5-ethyl*-1 : 6-*dihydro-6-pyrimidone*, prisms, m. p. 281—282° (decomp.); *hydrobromide*, needles, m. p. 160—175°, according to rate of heating; *hydrochloride*, m. p. 115°, crystallises with one H_2O.

Boiling hydrochloric acid converts 6-amino-2-ethylthiol-4-methyl-5-ethylpyrimidine into 6-*amino-4-methyl-5-ethyl-2* : 3-*dihydro-2-pyrimidone* (*methylethylcytosine*), $CO \diagdown_{NH-CMe}^{N:C(NH_2)} \diagup CEt$, blocks or rectangular prisms, m. p. 295° (decomp.), which is obtained first as the *hydrochloride*, a colourless powder, decomp. at 125°; the *hydrobromide*, blocks, decomp. near 260°; the *picrate*, needles, *mercurichloride*, *phosphotungstate*, and *potassio-bismutho-iodide* were also prepared.

The sodium salt of 2-thio-4-methyluracil reacts with diphenylmethyl bromide in alcoholic solution with formation of 2-*diphenylmethylthiol-4-methyl*-1 : 6-*dihydro-6-pyrimidone*, $CH \diagdown_{CMe-N}^{CO \cdot NH} \diagup C \cdot S \cdot CHPh_2$, m. p. 214°, in small yield.   D. F. T.

Hydantoins. XXIII. Synthesis of 2-Thiohydantoins from Acyl Derivatives of α-Amino-acids. TREAT B. JOHNSON and WALTER M. SCOTT (*J. Amer. Chem. Soc.*, 1913, **35**, 1130—1136. Compare Johnson, A., 1912, i, 390; Johnson and Nicolet, A., 1912, i, 53, etc.). —The reaction between ammonium thiocyanate and an acyl derivative

of an α-amino-acid in acetic anhydride solution appears to be a general one, but the only β-amino-acid examined merely underwent acetylation without any subsequent reaction with the thiocyanate.

o-Carboxybenzoylaminoacetic acid, $CO_2H \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, obtained by the hydrolysis of ethyl phthalylaminoacetate, when heated by steam for twenty minutes with a $1\frac{1}{4}$ molecular proportion of ammonium thiocyanate in 5—7 parts by weight of acetic anhydride, gave 2-thiohydantoin, m. p. 225—227°, phthalylaminoacetic acid, m. p. 192—193°, and phthalic acid. This was the only case in which the acylhydantoin could not be isolated, although the results indicate that it must have been an intermediate product of the reaction.

p-Methoxyhippuric acid with ammonium thiocyanate in acetic anhydride solution gave 3-p-*methoxybenzoyl-2-thiohydantoin*,

$$\begin{array}{c} CO \cdot CH_2 \\ NH - CS \end{array}\!\!\!\!> N \cdot CO \cdot C_6H_4 \cdot OMe,$$
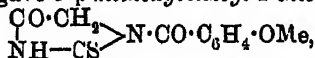
pale yellow prisms, m. p. 166°, whilst m-nitrohippuric acid yielded 3-m-*nitrobenzoyl-2-thiohydantoin*, m. p. 198—199°.

Benzenesulphonylaminoacetic acid in an analogous manner gave rise to 3-*benzenesulphonyl-2-thiohydantoin*, $\begin{array}{c} CO \cdot CH_2 \\ NH - CS \end{array}\!\!\!\!> N \cdot SO_2Ph$, colourless needles, m. p. 210—211° (decomp.).

The product obtained by a similar process with carbethoxyamino-acetic acid was ethyl 2-thiohydantoin-3-carboxylate, $\begin{array}{c} CO \cdot CH_2 \\ NH - CS \end{array}\!\!\!\!> N \cdot CO_2Et$, plates, m. p. 168°.

The application of dibromophenylalanine and benzoylalanine to this reaction resulted in the formation of 2-*thio-3-acetyl-4-dibromobenzyl-hydantoin*, $\begin{array}{c} NH - CO \\ CS \cdot NAc \end{array}\!\!\!\!> CH \cdot CH_2 \cdot C_6H_3Br_2$, plates, m. p. 171° (which on hydrolysis gave 2-*thio-4-dibromobenzylhydantoin*, colourless needles, m. p. 243°), and 2-*thio-3-benzoyl-4-methylhydantoin*, m. p. 158° respectively.

Anthranilic acid under similar treatment merely became converted into acetylanthranilic acid. D. F. T.

Hydantoins. XXIV. Action of Ammonium Thiocyanate on Lactone Anhydrides of Acylamino-acids. TREAT B. JOHNSON and WALTER M. SCOTT (*J. Amer. Chem. Soc.*, 1913, **35**, 1136—1143. Compare preceding abstract).—The provisional interpretation of the mechanism of the reaction between thiocyanic acid (as ammonium thiocyanate) and the acyl derivative of a monobasic α-amino-acid in acetic anhydride (Johnson and Nicolet, A., 1912, i, 53) is withdrawn in favour of the scheme :

$$RCO \cdot NH \cdot CH_2 \cdot CO_2H \xrightarrow{Ac_2O} \begin{array}{c} CR:N \\ O \cdot CO \end{array}\!\!\!\!> CH_2 \xrightarrow{HSCN}$$

$$RCO \cdot NH \cdot CH_2 \cdot CO \cdot NCS \rightarrow \begin{array}{c} NH - CS \\ CO \cdot CH_2 \end{array}\!\!\!\!> N \cdot COR.$$
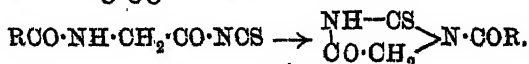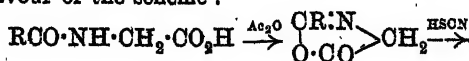
Among the reasons for this new view are the facts that acetic anhydride is the only solvent which has been found suitable, and that

the first ring formation is a normal change when acylamino-acids are heated with acetic anhydride; it has already been shown that the lactonoid anhydrides undergo scission by hydrogen chloride, producing acid chlorides in a manner analogous to the second change above (compare Mohr and Kohler, A., 1910, i, 116).

In agreement with the above explanation it is found that with hippuric acid or benzoylalanine, acylthiohydantoins are not produced in acetic acid with ammonium thiocyanate, although if the amino-acid is previously heated with acetic anhydride the resulting lactonoid anhydride readily gives rise to the corresponding acylthiohydantoin in acetic acid solution.

Acetylphenylglycine and ethyl hippurate are not affected by ammonium thiocyanate in acetic anhydride, thus indicating the necessity for the presence of unsubstituted hydrogen at the nitrogen atom and at the carboxyl group. With benzamide, no evidence of the formation of benzoylthiocarbamide was obtained; this is a further reason for discarding the old theory of formation in favour of that now suggested.

Contrary to expectation, the lactim of a-benzoylamino-β-phenyl-acrylic acid failed to react with thiocyanic acid in acetic anhydride, whilst the free acid under such treatment only yielded the lactim.

<div align="right">D. F. T.</div>

Rings Containing a Triple Linking. II. Optimum Number of Atoms in the Ring. PAUL RUGGLI (*Annalen*, 1913, **399**, 174—182).—The following substances of the type

$$O_6H_4 \underset{\hspace{2.5em}C{:}O}{\overset{NH{\cdot}CO{\cdot}[CH_2]x{\cdot}CO{\cdot}NH}{<\hspace{4em}>}} O_6H_4$$
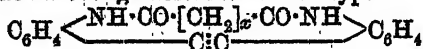
have been prepared from oo'-diaminotolan and the requisite acid chloride in the same manner as *cyclo*succinyldiaminotolan (A., 1912, i, 914); *cyclo*glutaryldiaminotolan, $C_{19}H_{16}O_2N_2$, m. p. 300—302° (decomp.), colourless crystals, *cyclo*adipyldiaminotolan, $C_{20}H_{18}O_2N_2$, m. p. 252° (decomp.), colourless needles, *cyclo*pimelyldiaminotolan, $C_{21}H_{20}O_2N_2$, m. p. 248° (decomp.), colourless needles, *cyclo*suberyldiaminotolan, $C_{22}H_{22}O_2N_2$, m. p. 223—224·5°, colourless needles, and *cyclo*lepargyldiaminotolan, $C_{23}H_{24}O_2N_2$, m. p. about 240° (decomp.), colourless needles.

A comparison of the yields obtained under similar conditions shows *cyclo*adipyldiaminotolan, containing a 14-membered ring, is obtained in the largest amount, namely, 50% of that theoretically possible. Cyclic compounds containing a nuclear triple linking have not been obtained from pp'-diaminotolan or from *trans*-oo'-diaminostilbene.

pp'-Dinitrotolan, which is best prepared by boiling pp'-dinitrostilbene dibromide with pyridine, is readily reduced to pp'-diaminotolan by stannous chloride and hydrochloric and acetic acids in the cold.

<div align="right">C. S.</div>

Benzylcreatinine. WILLY HENNIG (*Arch. Pharm.*, 1913, **251**, 396—400).—Creatinine and benzyl chloride at 136—140° yield *benzylcreatinine hydrochloride*, $C_{11}H_{13}ON_3,HCl$, faintly yellow needles, blackening at about 230° (*aurichloride*, $C_{11}H_{13}ON_3,HAuCl_4$, m. p. 158°, yellow needles; *platinichloride*, $2C_{11}H_{13}ON_3,H_2PtCl_6$, m. p.

177—178°, red crystals), from an aqueous solution of which lead hydroxide liberates *benzylcreatinine*, m. p. 225°, faintly yellow crystals. The action, therefore, of benzyl chloride, similarly to that of alkyl iodides, on creatinine is substitutive, not additive. The oxidation of benzylcreatinine hydrochloride by alkaline 5% potassium permanganate at 30—40° yields *benzylmethylguanidine* (*platinichloride*,

$$2C_9H_{10}N_3,H_2PtCl_6,$$
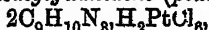
m. p. 148°; *aurichloride*, m. p. 190—191°). C. S.

Addition of Phenylazoimide to Quinones. II. LUDWIG WOLFF (*Annalen*, 1913, **399**, 274—297).—[With R. HERCHER.]— a-Naphthaquinone and phenylazoimide react to form a dihydrotriazole derivative, $C_6H_4\big<^{CO\cdot CH\cdot NPh}_{CO\cdot CH-\!-N}\big>N$, which cannot be isolated, but decomposes, yielding mainly 1-*phenylazoimino-a-naphthaquinone* [4 : 9-*diketo-1-phenyldihydro-ββ-naphtha*iso*triazole*],

$$C_6H_4\big<^{CO\cdot C\cdot NPh}_{CO\cdot C-\!-N}\big>N,$$
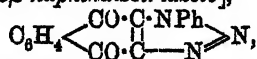
m. p. 241°, pale yellow leaflets, at 60—65°, and mainly *indandione-2-aldehydeanil*, $C_6H_4\big<^{CO}_{CO}\big>CH\cdot CH:NPh$, m. p. 191°, yellow prisms or plates, on the water-bath.

Phenylazoiminonaphthaquinone forms an *oxime*,

$$C_6H_4\big<^{C(:NOH)\cdot C\cdot NPh}_{CO-\!-\!-C-\!-N}\big>N,$$
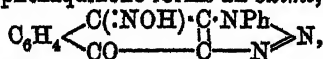
m. p. 232° (decomp.), almost colourless needles, which probably contains the oximino-group in the position shown, because, unlike the parent substance, it is not ruptured by sodium hydroxide. Phenylazoiminonaphthaquinone itself is decomposed by boiling aqueous alcoholic sodium hydroxide, yielding after acidification 4-o-*carboxybenzoyl-1-phenyl-1* : 2 : 3-*triazole*, $CO_2H\cdot C_6H_4\cdot CO\cdot C\big<^{CH\cdot NPh}_{N\!=\!N}$, m. p. 177—178° (anhydrous), colourless needles containing $\frac{1}{2}H_2O$. This acid is decomposed into phthalic acid, aniline, and probably acetic acid by aqueous sodium hydroxide at 150°, and in alkaline solution yields with hydroxylamine hydrochloride and subsequent acidification the oxime of the acid, which, however, slowly changes to an *anhydride*, $C_{16}H_{10}O_2N_4$, m. p. 220°, colourless needles, insoluble in sodium carbonate.

Indandione-2-aldehydeanil does not develop a coloration with ferric chloride, forms a *sodium* salt, red needles, with alcoholic sodium hydroxide, and is decomposed by boiling aqueous sodium hydroxide, yielding aniline and indandione-2-aldehyde in the form of its *sodium* salt, $C_{10}H_5O_3Na$, yellow needles. Indandione-2-aldehyde crystallises in colourless needles containing H_2O, m. p. 125° (decomp.) (141°, anhydrous), develops a red coloration with ferric chloride, and behaves like a strong, monobasic acid, decomposing carbonates; the *calcium* salt crystallises in sparingly soluble prisms. The aldehyde or its salt in cold aqueous solution reacts with aniline, phenylhydrazine, hydroxylamine, and semicarbazide to form respectively the preceding anil;

phenylhydrazone, $C_{16}H_{12}O_2N_2$, m. p. 220° (decomp.), yellow prisms; *oxime*, $C_{10}H_7O_8N,H_2O$, m. p. 205° (decomp.), orange needles, and *semicarbazone*, $C_{11}H_9O_2N_3$, m. p. 233° (decomp.), yellow needles.

By boiling with 20% hydrochloric acid, the sodium salt of indandione-2-aldehyde is decomposed into formic acid, bindone, indandione, and a *substance*, $C_{19}H_{10}O_4$, m. p. about 308° (decomp.), red needles, which is probably $C_6H_4\!\!<\!\!^{CO}_{CO}\!\!>\!\!C\!:\!CH\cdot CH\!\!<\!\!^{CO}_{CO}\!\!>\!\!C_6H_4$, since it can also be produced by heating equal molecular quantities of indandione and its aldehyde at 120° or in boiling alcohol, and can be converted into these two substances by aqueous sodium hydroxide.

[With M. Körbs.]—Three of the four substances produced by the interaction of phenylazoimide and *p*-benzoquinone have been previously described (A., 1912, i, 1034). The fourth is a *substance*, $C_{18}H_{14}O_2N_4$, m. p. 157—160° (decomp.), yellow leaflets, the constitution of which has not yet been entirely established. The author recommends the formula $N\!\!<\!\!^{NPh\cdot CH\cdot CO}_{N——CH\cdot CO}\!\!>\!\!CH\cdot CH\!:\!NPh$, according to which the substance is the *anil* of *phenylazoiminopentionaldehyde*. The absence of an imino-group and the presence of a triazole ring are respectively proved by the inactivity of the substance towards phenylcarbimide and by the oxidation of the sodium salt of phenylazoiminopentionaldehyde to 1-phenyl-1 : 2 : 3-triazole-4-carboxylic acid and 1-phenyl-1 : 2 : 3-triazole-5-carboxylic acid by 2% sodium hypobromite at 0°. The presence of the C_6-ring in the anil has not been proved, but is rendered very probable by the great similarity of the substance to the anil of indandione-2-aldehyde in its method of formation and behaviour.

By treatment with 10% potassium hydroxide and a little alcohol at 30—40°, the anil is converted into the *potassium* salt of phenylazo-iminopentionaldehyde, $C_{12}H_8O_2N_3K,\frac{1}{2}H_2O$, colourless prisms which become yellow in light; the *sodium* salt, $C_{12}H_8O_2N_3Na,H_2O$, crystallises in colourless leaflets, and forms a *semicarbazone*, $C_{18}H_{11}O_2N_6Na,2\frac{1}{2}H_2O$, faintly yellow needles. These salts and also the semicarbazone are extensively decomposed by treatment with even weak acids.

By fusion or by boiling with xylene or aniline, the anil of phenyl-azoiminopentionaldehyde loses nitrogen and yields a *substance*,
$$C_{18}H_{14}O_2N_2,$$
m. p. 185°, colourless needles, which behaves very similarly to the original anil and is, therefore, probably the *anil* of *phenyliminopention-aldehyde*, $NPh\!\!<\!\!^{CH\cdot CO}_{CH\cdot CO}\!\!>\!\!CH\cdot CH\!:\!NPh$. It does not react with phenylcarbimide or with ferric chloride, and is converted by boiling sodium hydroxide into aniline and the *sodium* salt of *phenyliminopen-tionaldehyde*, $C_{12}H_8O_2NNa,2H_2O$, white needles.

By keeping phenylazoiminopentionaldehydeanil in glacial acetic acid until the evolution of nitrogen ceases, a *substance*, $C_{18}H_{16}O_2N_2$, m. p. about 186° (decomp.), yellow, crystalline powder, is obtained, which is converted by hot aqueous alcoholic sodium hydroxide into aniline and the *sodium* salt of an *acid*, $C_{12}H_9O_2N$, m. p. 234°, colourless needles.

3 : 6-Diamino-1 : 2 : 4 : 5-tetrazine. I. Giacomo Ponzio and G. Gastaldi (*Gazzetta*, 1913, 43, ii, 129—137).—3 : 6-*Diamino*-1 : 2 : 4 : 5-*tetrazine*, $H_2N \cdot C \underset{N \cdot N}{\overset{N : N}{<}} > C \cdot NH_2, H_2O$, begins to crystallise in a few days when a mixture of concentrated solutions of aminoguanidine hydrochloride and potassium hydroxide are kept over concentrated sulphuric acid and solid potassium hydroxide. The substance crystallises in reddish-violet, monoclinic needles, which have a metallic lustre, or in amethyst-coloured laminæ. On heating, it loses water at about 100°, and melts at 204—205° (decomp.), or 206—207° (decomp.), according to the mode of heating; cyanogen and ammonia are evolved. When boiled with sulphuric acid, it yields nitrogen, carbon dioxide, and hydrazine sulphate, whilst heating with potassium hydroxide furnishes ammonia. It is readily reduced to 3 : 6-diamino-1 : 2-dihydro-1 : 2 : 4 : 5-tetrazine. 3 : 6-*Diamino*-1 : 2 : 4 : 5 - *tetrazine hydrochloride*, $C_2H_4N_6$,HCl, forms orange-yellow laminæ, and decomposes about 200°; the *nitrate*, $C_2H_4N_6$,HNO_3,$\frac{1}{2}H_2O$, crystallises similarly, and has m. p. 180—182° (decomp.). The *oxalate*,

$$(C_2H_4N_6)_2, H_2C_2O_4,$$

forms orange prisms, which decompose at about 205°. R. V. S.

Action of Dichlorocarbamide on Amines. Synthesis of 3-Hydroxy - 6- keto-3-phenyl - 2 : 4 - dibenzyl - 1 : 2 : 4 : 5 - tetrazine. Rasik Lal Datta and Satyaranjan Das Gupta (*J. Amer. Chem. Soc.*, 1913, 35, 1183—1185).—By modifying the conditions for the interaction of dichlorocarbamide and amines, which has already been shown to yield chloroamines (Datta, T., 1912, 101, 166 ; A., 1912, i, 962), it is found that other substances can be isolated from the reaction product.

When a cooled saturated solution of dichlorocarbamide is added to a cooled fairly strong aqueous solution of allylamine, a small amount of *p*-urazine separates.

On applying benzylamine in a similar reaction the crystalline product which deposits is a mixture of *p*-urazine with 3-hydroxy-6-keto-3-phenyl-2 : 4-dibenzyl-1 : 2 : 4 : 5-tetrazine. The latter, which can be separated by its greater solubility in acetone, probably owes its formation to the primary formation of benzylchloroamine, two molecules of which then condense with one of free benzylamine and one of dichlorocarbamide. D. F. T.

The Solubility of Uric Acid in Acetic Acid. Francesco Rossi (*Biochem. Zeitsch.*, 1913, 54, 297—304).—The solubility of uric acid in varying strengths of acetic acid from $N/100$ to $16N$ (glacial acetic acid) and at temperatures varying from 15° to 100° was determined. Between the concentrations $N/100$ and $N/10$ the solubility is less than in water ; above the latter concentration it increases and reaches a maximum somewhere about the concentration of $4N$ to $6N$; in higher concentrations, the solubility again declines, especially at higher temperatures. The latter phenomenon is probably due to an action of acetic acid on the uric acid. S. B. S.

Some New Derivatives of Azoxybenzene. BRUNO VALORI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 125—133. Compare Angeli and Valori, A., 1913, i, 533).—When Zinin's *p*-nitroazoxybenzene is treated with nitric acid (D 1·48) on the water-bath, 2 : 4-*dinitroazoxybenzene*, $C_6H_3(NO_2)_2 \cdot N{:}NPh{:}O$, is produced; it forms pale yellow needles, m. p. 141°.

When Zinin's *p*-nitroazoxybenzene is heated with bromine in presence of iron for one hour at 130° in a sealed tube, 2-*bromo*-4-*nitroazoxybenzene*, $NO_2 \cdot C_6H_3Br \cdot N{:}NPh{:}O$, is formed; it is a yellow powder, m. p. 127°.

o-Nitroazoxybenzene is acted on by nitric acid (D 1·48) on the water-bath, yielding 2 : 6-*dinitroazoxybenzene*, $C_{12}H_8O_5N_4$, which forms colourless scales, m. p. 172°.

If *o*-*p*-bromoazoxybenzene is heated with bromine in presence of iron in a sealed tube for two hours at 115—120°, 2 : 4-*dibromoazoxybenzene*, $C_{12}H_8ON_2Br_2$, is formed; it crystallises in yellow needles, m. p. 97°. In its preparation a small quantity of 2 : 4 : 6-tribromoaniline is produced. Reduction of 2 : 4-dibromoazoxybenzene with tin and hydrochloric acid yields aniline and 2 : 4-dibromoaniline. 2 : 4-Dibromoazoxybenzene yields 2 : 4-*dibromoazobenzene*, $C_{12}H_8N_2Br_2$, when treated with concentrated sulphuric acid, or when reduced with aluminium amalgam and subsequently oxidised with yellow mercury oxide. 2 : 4-Dibromoazobenzene forms orange-red prisms, m. p. 96°. It regenerates the azoxy-compound when treated with hydrogen peroxide in glacial acetic acid solution. 2 : 4 : 4'-*Tribromoazobenzene*,
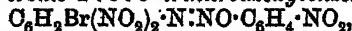
$$C_{12}H_7N_2Br_3,$$
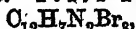
can be obtained by warming dibromoazobenzene with bromine and iron for a few minutes on the water-bath; it is a pale red substance, m. p. 146°. On oxidation with hydrogen peroxide in glacial acetic acid solution, this compound yields the corresponding 2 : 4 : 4'-*tribromoazoxybenzene*, which on reduction with aluminium amalgam and subsequent oxidation with yellow mercury oxide yields the tribromoazo-compound again. 2 : 4 : 4'-Tribromoazoxybenzene, $C_{12}H_7ON_2Br_3$, crystallises in yellow needles, m. p. 154°.

When 4-bromo-2-nitroazoxybenzene (m. p. 99°) is heated on the water-bath with nitric acid (D 1·50) two products are obtained: (1) 4-*bromo*-2 : 6-*dinitroazoxybenzene*, which forms very pale yellow needles, m. p. 163°, and on treatment with concentrated sulphuric acid yields the isomeric *hydroxyazo*-compound,

$$C_6H_2Br(NO_2)_2 \cdot N{:}N \cdot C_6H_4 \cdot OH$$
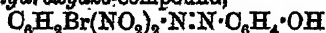
(m. p. 224°); (2) 4-*bromo*-2 : 6 : 3'-*trinitroazoxybenzene*,

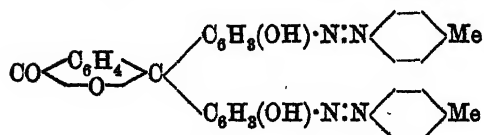$$C_6H_2Br(NO_2)_2 \cdot N{:}NO \cdot C_6H_4 \cdot NO_2,$$

which is a yellowish-green, crystalline powder, m. p. 209° (decomp.). The latter compound is exclusively formed if stronger acid (D 1·52) is used in the reaction.   R. V. S.

Phthaleïns. II. Some Nitrogenous Derivatives of Phenolphthaleïn and the Constitution of its Salts. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 175—190. Compare Oddo and Vassallo, A., 1912, i, 792).—*Bis*-p-*tolueneazophenolphthaleïn* (formula overleaf) is obtained when a diazotised solution of *p*-toluidine (1 mol.) is poured

into a cold solution of phenolphthalein ($\frac{1}{2}$ mol.) in potassium hydroxide (3 mols.). It is an orange-yellow, crystalline substance, m. p. 249—253°. When the mother-liquor is acidified, a bright red substance, m. p. 207—210°, is precipitated; the *acetyl* derivative of this compound forms pale yellow scales, m. p. 148—150°. The *diacetyl* derivative of bis-*p*-tolueneazophenolphthalein, $C_{38}H_{30}O_6N_4$, has m. p. 125—131°.

$$CO<\overset{C_6H_4}{\underset{O}{}}>C<\overset{C_6H_3(OH)\cdot N\colon N<\text{—}>Me}{\underset{C_6H_3(OH)\cdot N\colon N<\text{—}>Me}{}}$$

Bis-o-nitrobenzeneazophenolphthalein, $C_{32}H_{20}O_8N_6$, is an orange-yellow substance, m. p. 277°. Its *diacetyl* derivative has m. p. 124—129°. In the preparation of bis-*o*-nitrobenzeneazophenolphthalein, a *substance* of similar appearance but different solubility is formed; its *acetyl* derivative has m. p. 169°.

When bis-*p*-tolueneazophenolphthalein is heated to 110° with phenylhydrazine, a reaction occurs, which is accompanied by rise of temperature and yields diaminophenolphthalein,

$$CO<\overset{C_6H_4}{\underset{O}{}}>C\colon[C_6H_3(NH_2)\cdot OH]_2,$$
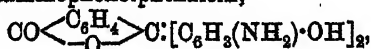
which forms pale coffee-coloured crystals, m. p. 245° (decomp.). The substance dissolves in alkalis, alkali carbonates and ammonia, giving a Prussian-blue coloration which disappears on acidification. The substance gives the same coloration with aqueous solutions of pyridine, but not with alcoholic solutions. Diaminophenolphthalein can also be obtained by reduction of dinitrophenolphthalein with stannous chloride (compare Errera and Berté, A., 1896, i, 564; Gattermann and Bamberg, A., 1899, i, 514).

Dinitrophenolphthalein yields a *monoacetyl* derivative, $C_{24}H_{16}O_{10}N_2$, which has m. p. 94—100°, and occurs in a white and in a yellow form.

R. V. S.

Mechanism of Formation and Scission of the Hydroxyazo-compounds. G. CHARRIER and G. FERRERI (*Gazzetta*, 1913, 43, ii, 148—162. Compare this vol., i, 535).—When an ethereal solution of nitric acid (prepared by adding about 20% of nitric acid [D 1·48] to ether cooled in ice) is added to an ethereal solution of 1-benzeneazo-2-naphthyl methyl ether, the *nitrate* of the ether, $C_{17}H_{14}ON_2,2HNO_3$, separates in red, silky needles, m. p. 67° (decomposing with evolution of gas at 69—70°). The salt has about the normal molecular weight in boiling chloroform. It is hydrolysed by water. The salt readily decomposes into benzenediazonium nitrate and 1-nitro-2-naphthyl methyl ether.

The *nitrate* of 1-benzeneazo-2-naphthyl ethyl ether,

$$C_{18}H_{16}ON_2,2HNO_3,$$
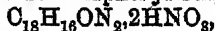
forms quadrangular tablets, which are green by reflected and red by transmitted light, and have m. p. 80—81° (decomp.). It readily decomposes in an analogous manner to the methyl ether nitrate.

When 1-nitro-2-naphthyl ethyl ether is warmed with nitric acid

(D 1·40), it is converted quantitatively into 1 : 6-dinitro-2-naphthyl ethyl ether.

A dark red, crystalline crust, consisting probably of 1-benzeneazo-2-naphthol nitrate, is obtained after mixing ethereal nitric acid with an ethereal solution of 1-benzeneazo-2-naphthol. The substance is very unstable.

$$C_{10}H_6 \begin{cases} N{:}NHPh{\cdot}ONO_2 \\ ONO_2 \\ O{\Leftarrow}H \\ R \end{cases}$$
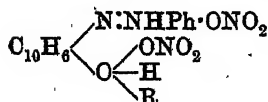
The probable structure of these salts is indicated by the annexed formula, and their mode of decomposition mentioned above suggests an analogous mechanism of formation and scission of the hydroxyazo-compounds.

R. V. S.

Etherification of *o*-Hydroxyazo-compounds. III. G. CHARRIER and G. FERRERI (*Gazzetta*, 1913, 43, ii, 211—227. Compare A., 1912, i, 812; this vol., i, 535, and preceding abstract).—In this paper further nitrates of ethers of arylazo-β-naphthols are described. Their chemical and physical properties resemble those of the members already described (*loc. cit.*).

1-*o*-*Tolueneazo-2-naphthyl methyl ether nitrate*, $C_{18}H_{16}ON_2,2HNO_3$, forms cantharides-green, acicular crystals, m. p. 71° (decomp.).

1-*o*-*Tolueneazo-2-naphthyl ethyl ether nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, crystallises in cantharides-green leaflets, m. p. 62—63° (decomp.).

1-*m*-*Tolueneazo-2-naphthyl methyl ether nitrate*, $C_{18}H_{16}ON_2,2HNO_3$, crystallises similarly, and has m. p. 72° (decomp.).

1-*m*-*Tolueneazo-2-naphthyl ethyl ether nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, forms cantharides-green leaflets, m. p. 84° (decomp.).

1-*p*-*Tolueneazo-2-naphthyl methyl ether hydrochloride* forms red needles which have a golden lustre. The *hydrobromide* crystallises in metallic-looking, green leaflets. The *nitrate*, $C_{18}H_{16}ON_2,2HNO_3$, forms dark red needles with a green lustre, and has m. p. 77° (decomp.).

1-*p*-*Tolueneazo-2-naphthyl ethyl ether nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, crystallises in garnet-red leaflets of golden lustre, and has m. p. 94° (decomp.).

1-*o*-4-*Xyleneazo-2-naphthol*, $C_{18}H_{16}ON_2$, crystallises in cherry-red needles of golden lustre, m. p. 146°; it dissolves in concentrated sulphuric acid, producing an intense red coloration. The *methyl ether*, $C_{19}H_{18}ON_2$, crystallises in red, prismatic leaflets, m. p. 106°. The *methyl ether hydrochloride* forms red needles with golden lustre; the *hydrobromide*, garnet-red needles. The *nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, forms coffee-coloured scales of golden lustre, m. p. 87—88° (decomp.). The *ethyl ether*, $C_{20}H_{20}ON_2$, forms red needles of golden lustre, m. p. 94—95°. The *ethyl ether hydrochloride* forms metallic-looking, coffee-coloured needles; the *hydrobromide*, red needles.

1-*m*-4-*Xyleneazo-2-naphthyl methyl ether*, $C_{19}H_{18}ON_2$, forms garnet-red leaflets of violet lustre, m. p. 72—73°. The *hydrochloride* and *hydrobromide* form garnet-red, acicular crystals. The *nitrate*,

$$C_{19}H_{18}ON_2,2HNO_3,$$
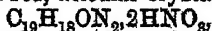
crystallises in cantharides-green needles, m. p. 83° (decomp.).

m-4-Xylenediazonium nitrate and 2-naphthylamine yield 1-*m*-4-*xylene*-

azo-2-naphthylamine, $C_{18}H_{17}N_3$, which crystallises in orange-red leaflets, m. p. 128°. The substance dissolves in concentrated sulphuric acid, producing a reddish-violet coloration.

1-m-4-*Xyleneazo-2-naphthyl ethyl ether*, $C_{20}H_{20}ON_2$, forms garnet-red needles, m. p. 47°. The *hydrochloride* forms coffee-coloured needles, and the hydrobromide, garnet-red needles. The *nitrate*,

$$C_{20}H_{20}ON_2,2HNO_3,$$

crystallises in cantharides-green needles, m. p. 82° (decomp.).

1-p-*Xyleneazo-2-naphthyl methyl ether*, $C_{19}H_{18}ON_2$, forms garnet-red, prismatic tablets, m. p. 91—92°. The *hydrochloride* crystallises in garnet-red needles; the *hydrobromide* in coffee-coloured needles. The *nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, crystallises in cantharides-green laminæ, m. p. 75° (decomp.). The *ethyl ether*, $C_{20}H_{20}ON_2$, crystallises in tufts of red needles or laminæ, m. p. 61—62°. The *hydrochloride* forms a crust of copper-coloured needles, and the *hydrobromide* crystallises similarly. The *nitrate*, $C_{20}H_{20}ON_2,2HNO_3$, forms dark copper-coloured laminæ of golden lustre, m. p. 71° (decomp.).

1-*a-Naphthaleneazo-2-naphthyl methyl ether hydrobromide* crystallises in iridescent, brownish-green needles. R. V. S.

Etherification of *o*-Hydroxyazo-compounds. IV. G. CHARRIER and G. FERRERI (*Gazzetta*, 1913, **43**, ii, 227—244. Compare preceding abstracts).—1-*Anisoleazo-2-naphthyl methyl ether hydrobromide* forms reddish-brown needles. The *nitrate*, $C_{18}H_{16}O_2N_2.2HNO_3$, forms dark green needles, m. p. 90—91° (decomp.). 1-*Anisoleazo-2-naphthylamine*, $C_{17}H_{15}ON_3$, crystallises in garnet-red prisms, m. p. 133—134°; it is soluble in concentrated sulphuric acid with production of a reddish-violet coloration.

1-*Anisoleazo-2-naphthyl ethyl ether hydrobromide* forms brownish-red needles. The *nitrate*, $C_{19}H_{18}O_2N_2,2HNO_3$, is a dark green, crystalline substance, m. p. 85° (decomposing at 86—87°).

1-p-*Methoxybenzeneazo-2-naphthyl methyl ether hydrobromide* forms cantharides-green needles. The *nitrate*, $C_{18}H_{16}O_2N_2,2HNO_3$, forms green, acicular crystals, m. p. 55—56° (decomp.). 1-p-*Methoxybenzeneazo-2-naphthylamine*, $C_{17}H_{15}ON_3$, crystallises in garnet-red leaflets, m. p. 127°. It dissolves in concentrated sulphuric acid, giving a violet-red coloration.

1-p-*Methoxybenzeneazo-2-naphthyl ethyl ether hydrobromide* forms coffee-coloured needles. The *nitrate*, $C_{19}H_{18}O_2N_2,2HNO_3$, crystallises in cantharides-green leaflets, m. p. 67° (decomp.).

1-o-*Ethoxybenzeneazo-2-naphthyl methyl ether hydrochloride* forms garnet-red crystals; the *hydrobromide*, coffee-coloured needles. The *nitrate*, $C_{19}H_{18}O_2N_2,2HNO_3$, crystallises in dark red leaflets of metallic lustre.

1-o-*Ethoxybenzeneazo-2-naphthyl ethyl ether hydrobromide* forms brown needles; the *nitrate*, $C_{20}H_{20}O_2N_2,2HNO_3$, crystallises in green needles, m. p. 86° (decomp.). 1-o-*Ethoxybenzeneazo-2-naphthylamine*, $C_{18}H_{17}ON_3$, forms bright red leaflets, m. p. 117°. It dissolves in concentrated sulphuric acid, giving a reddish-violet coloration.

1-p-*Ethoxybenzeneazo-2-naphthyl methyl ether hydrobromide* forms

coffee-coloured needles. The *nitrate*, $C_{10}H_{18}O_2N_2,2HNO_3$, forms green needles, m. p. 71° (decomp.). 1-p-*Ethoxybenzeneazo-2-naphthylamine*, $C_{18}H_{17}ON_3$, crystallises in orange-yellow laminæ of golden lustre, m. p. 133—134°.

1-p-*Ethoxybenzeneazo-2-naphthyl ethyl ether hydrobromide* forms golden leaflets. The *nitrate*, $C_{20}H_{20}O_2N_2,2HNO_3$, forms orange-yellow plates of golden lustre, m. p. 73—74° (decomp.).

1-o-*Nitrobenzeneazo-2-naphthyl methyl ether*, $C_{17}H_{13}O_3N_3$, crystallises in garnet-red leaflets, m. p. 136—137°. It dissolves in concentrated sulphuric acid, giving an intense red coloration. The *hydrochloride* forms coffee-coloured needles, and the *hydrobromide* is a pale coffee-coloured, crystalline substance. The *nitrate*, $C_{17}H_{13}O_3N_3,2HNO_3$, forms red crystals, m. p. 103°.

1-o-*Nitrobenzeneazo-2-naphthyl ethyl ether*, $C_{18}H_{15}O_3N_3$, crystallises in thin, dark red tablets, m. p. 111°. The *hydrochloride* and the *hydrobromide* are red, crystalline substances. The *nitrate*,

$$C_{18}H_{15}O_3N_3.2HNO_3,$$

forms dark red leaflets of metallic lustre, m. p. 105° (decomp.).

1-m-*Nitrobenzeneazo-2-naphthyl methyl ether nitrate*,

$$C_{17}H_{13}O_3N_3,2HNO_3,$$

consists of golden leaflets, m. p. 66—68° (decomp.).

1-m-*Nitrobenzeneazo-2-naphthyl ethyl ether hydrobromide* is a red, crystalline substance. The *nitrate*, $C_{18}H_{15}O_3N_3,2HNO_3$, crystallises in golden leaflets, m. p. 70° (decomp.).

1-p-*Nitrobenzeneazo-2-naphthyl methyl ether*, $C_{17}H_{13}O_3N_3$, forms dark red, iridescent leaflets, m. p. 128—129°. The *hydrochloride* is a red, and the *hydrobromide* a coffee-coloured, crystalline substance. The *nitrate*, $C_{17}H_{13}O_3N_3,2HNO_3$, forms cantharides-green leaflets, m. p. 75° (decomp.).

1-p-*Nitrobenzeneazo-2-naphthyl ethyl ether*, $C_{18}H_{15}O_3N_3$, crystallises in dark red leaflets, m. p. about 186°. The *hydrochloride* and the *hydrobromide* are red, crystalline substances. The *nitrate*,

$$C_{18}H_{15}O_3N_3,2HNO_3,$$

forms cantharides-green leaflets, m. p. 95—97° (decomp.).

1-α-*Naphthaleneazo-2-naphthyl ethyl ether hydrobromide* crystallises in cantharides-green needles. The *nitrate*, $C_{22}H_{18}ON_2,2HNO_3$, crystallises in copper-red, flat needles of metallic lustre, m. p. 62° (decomp.).

1-β-*Naphthaleneazo-2-naphthyl methyl ether hydrobromide* crystallises in coffee-coloured needles. The *nitrate*, $C_{21}H_{16}ON_2,2HNO_3$, forms deep green, lustrous needles, m. p. 80—81° (decomp.).

Diphenyl-4 : 4'-bisazo-2-naphthol,

$$HO\cdot C_{10}H_6\cdot N\dot{:}N\cdot C_6H_4\cdot C_6H_4\cdot N\dot{:}N\cdot C_{10}H_6\cdot OH,$$

is a dark green, microcrystalline powder, m. p. about 275°; it dissolves in concentrated sulphuric acid with production of a violet-blue coloration. Its *diethyl ether*, $C_{36}H_{30}O_2N_4$, is a red, microcrystalline powder, m. p. about 98—100°. It is soluble in concentrated (and to some extent also in dilute) acids with production of a bluish-violet coloration. The *hydrochloride* and the *hydrobromide* are dark green, crystalline substances. The *nitrate*, $C_{36}H_{30}O_2N_4,4HNO_3$, forms dark green needles of metallic lustre, m. p. 60—61°.

R. V. S.

The Conjugation of the Products of Protein Hydrolysis to Colloidal Carbohydrates. H. FRIEDENTHAL (*Biochem. Zeitsch.*, 1913, **54**, 174—181).—Attention is called to the fact that by the condensation of hydroxyl groups in polysaccharides of colloidal character with the amino-groups of amino-acids, it is theoretically possible to obtain derivatives which have the same empirical composition as proteins, and should yield the same reactions. Although it is not claimed that the majority of the proteins is constituted in this way, it is suggested that substances of this character may exist in the organism. S. B. S.

Coagulation of Proteins by Ultra-violet Light. W. T. BOVIE (*Science*, 1913, **37**, 24—25).—Exposure of certain proteins in quartz tubes to the rays of a quartz mercury-vapour lamp causes them to coagulate. Usually no coagulum forms in glass tubes, but dialysed crystallised egg-albumin is sensitive to longer wave-lengths than the fresh egg-white, since it coagulates in a glass tube. The coagulum has the same properties as that produced by heat without exposure to ultra-violet light. E. F. A.

Temperature-coefficient of the Coagulum Caused by Ultra-violet Light. W. T. BOVIE (*Science*, 1913, **37**, 373—375).—Two reactions are involved in the coagulation of proteins by light: the chemical change caused by the light, and the production of a visible coagulum. The light reaction, resembling other photochemical changes, has a very low temperature-coefficient. The chemical change producing the visible coagulum has a temperature-coefficient as high as two. Probably similar relations exist in other physiological processes which result from the action of light. E. F. A.

The Precipitation of Colloids. II. KARL SPIRO (*Biochem. Zeitsch.*, 1913, **54**, 155—158. Compare A., 1904, i, 124).—A table is given showing that salts, of which the hydrogen-ion concentration in solution is highest, have the greatest action in inhibiting the precipitation of proteins. The hydrogen-ion concentration of the mixtures of the salt and protein solutions is not the mean of the two, but in the case of the sodium, potassium, and lithium salts it is nearly the same as that of the original protein solutions, and in the case of the ammonium salts a little greater. The acetates form an exception, in that the hydrogen-ion concentration of the mixture of protein–salt solutions approaches very nearly the [H˙]-concentration of the salt solution. The results seem to indicate the formation of a salt-protein compound, and the influence of salts on the precipitation of proteins is briefly discussed. S. B. S.

The Content of the Blood-Plasma Proteins in Basic Constituents. KARL LOCK and KARL THOMAS (*Zeitsch. physiol. Chem.*, 1913, **87**, 74—81).—The amounts of ammonia, arginine, histidine, and lysine in serum-albumin, serum-globulin, and fibrin were estimated and the table of results shows considerable discrepancies between

different preparations of the same protein, and according to the method used.   W. D. H.

The Soluble Protein Substances of Milk. Léon Lindet (*Compt. rend.*, 1913, **157**, 307—309).—The so-called albumin of milk possesses all the properties of caseinogen itself, with the exception of its rotatory power, where it has $[a]_D$ $-30°$ instead of $-116°$. The author suggests for it the name β-caseinogen, the a-caseinogen being the one, which is the chief constituent of the protein matter of milk. These two substances resemble one another closely in their solubility in milk serum, in their capillary adherence to the casein in suspension, in their precipitation by phenol, and in their partial coagulation at 75°.
                                                                W. G.

Influence of Calcium Chloride on the Curdling of Milk. Léon Lindet (*Compt. rend.*, 1913, **157**, 381—384. Compare preceding abstract).—Boiled milk is not clotted by rennet, but clots if a small amount of calcium chloride is added. This the author suggests is due to the interaction of the calcium chloride with the alkali phosphate and citrate in the milk serum, thus reducing the quantity of these, and rendering the two caseinogens less soluble. Further, the dicalcium phosphate by dissociation gives rise to phosphoric acid, which removes the calcium oxide from the caseinogens, rendering them still further insoluble.   W. G.

The Action of Rennin on Caseinogen. Alfred W. Bosworth (*J. Biol. Chem.*, 1913, **15**, 231—236).—Calcium caseinogenate which is neutral to litmus is not curdled by rennin ; but solutions which are acid and contain two equivalents of base for each molecule of caseinogen are curdled by rennin. Ammonium, sodium and potassium caseinogenates are not curdled by rennin. No other protein is formed except casein (2 molecules to one of caseinogen) during rennin curdling. Coagulation is the result of a change in solubility, and is the first stage in hydrolytic cleavage.   W. D. H.

Nucleohistone. I. Hermann Steudel (*Zeitsch. physiol. Chem.*, 1913, **87**, 207—213).—Nucleohistone prepared by the method given by Lilienfeld (A., 1894, ii, 146) had exactly the composition given previously. The whole of the nucleic acid present is proved to be true nucleic acid, no other substance containing phosphorus being present in nucleohistone.   E. F. A.

Processes Operative in Solutions, XXX, and Enzyme Action, XX. The Nature of Enzymes and of their Action as Hydrolytic Agents. E. Frankland Armstrong and Henry E. Armstrong (*Proc. Roy. Soc.*, 1913, B, **86**, 561—586).—A discussion of the problems of hydrolysis based on the experience gained in the course of two convergent series of enquiries.

The catalyst is defined as the agent which brings about the inclusion of the interacting substance in the circuit within which change takes place as soon as the circuit is established, the electrolyte being the

actual agent by which change is effected. Action between two non-electrolytes is impossible.

Enzymes are regarded as having a double function, namely, that of attracting or holding the hydrolyte and that of determining its hydrolysis. This twofold action is attributed to the presence in the enzyme of an acceptor together with an agent. The acceptor is a radicle very closely allied to a dominant group in the hydrolyte. The agent is an acid radicle in immediate or compatible proximity, so that a conducting path is formed between agent and acceptor by their association with the solvent. The efficiency of an enzyme depends also on its colloidal character. Each enzyme particle tends to absorb the hydrolyte, so that the solution at its surface is relatively concentrated; in addition it is hydrolated, the activity of the water molecules at the surface being greater than the average activity of the water. As a consequence the colloid surface remains highly charged with the hydrolyte probably up to the point at which the supply in the solution is exhausted.

The change is, therefore, not a simple mass action effect; in fact, in each successive interval of time the enzyme determines the hydrolysis of the same amount of hydrolyte. The observed departures from this rule are shown to be due to the influence of the products of change.

The relationship of the acceptor section of the enzyme to the hydrolyte is that of a superposable and, therefore, practically identical radicle.

The enzymes which hydrolyse the glucosides may be compounds of the glucoprotein class containing either α- or β-glucosidic radicles and therefore capable of hydrolysing either α- or β-glucosides, because their configuration harmonises with that of the one or of the other type of compound. Urease is an enzyme in which the urea residue in arginine is in suitable relationship with the carboxyl group. These conceptions are illustrated by photographs of solid models.

The resting enzyme is not an acid proper, but an internal salt of the glycine type. A substance of superior acidic power must be added to render the zymogen active. The action of acids and alkalis is considered from this point of view.

As the products of change accumulate in the solution, they affect the enzyme in various ways. The product immediately allied to the acceptor enters directly into competition with the hydrolyte. Other products act on the enzyme by neutralising it, by converting it into a derivative different in structure and no longer compatible with hydrolyte, or by changing the osmotic conditions in the solution, and altering the state of hydrolation at the colloid surface. These influences have been studied experimentally. E. F. A.

The Velocity of the Appearance of Protective Enzymes after Repeated Introduction of the Foreign Substrate. I. EMIL ABDERHALDEN and ERWIN SCHIFF (*Zeitsch. physiol. Chem.*, 1913, **87**, 225—230).—Whereas it takes some little time for the protective enzymes to appear on the first injection of a foreign peptone into the blood-serum, if a second injection is made, after the serum has become inactive again, the protective enzymes appear in a much

shorter time. The organism reacts much more rapidly to the second invasion. Experiments made on rabbits with silk peptone and gelatin peptone are described. The injection was preferably intravenous.

E. F. A.

Studies on the Specific Nature of the Intracellular Enzymes by means of the Optical Method. I. EMIL ABDERHALDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1913, **87**, 220—224).—The behaviour of the juices obtained from various macerated tissues after they had been completely deprived of blood was tested towards the peptones from each of the tissues. Whereas liver juice hydrolysed liver peptone, it had no action on kidney or thyroid peptone. Thyroid juice only attacked thyroid peptone. Kidney juice hydrolysed both kidney and liver peptones, and also, in one experiment out of three, it acted on thyroid peptone. The liver and thyroid cells contain enzymes adapted to their specific components only; the kidney cells have a wider function, and their enzymes are adapted to peptones from other sources.

E. F. A.

Enzymes of Fresh Foods. T. TADOKORO (*J. Coll. Agric. Sapporo, Japan*, 1913, **5**, 57—72).—The fresh sap of Udo twigs, yams, cabbage and lettuce leaves, onions, ginger and radish roots of Japanese origin has been investigated for enzymes. Peptolytic action was only found in ginger and the onion. All the juices contained trypsin and a weak diastase, also oxydase and catalase, but they differed greatly in activity. Lipase was present only in the cabbage. E. F. A.

Specific Nature of the Intracellular Enzymes by means of the Optical Method. II. EMIL ABDERHALDEN and ERWIN SCHIFF (*Zeitsch. physiol. Chem.*, 1913, **87**, 231—232).—The enzymes in muscle juice (from the horse) hydrolyse muscle peptone, but not liver or brain peptone.

Testicle peptone is hydrolysed only by the enzymes in testicle and kidney juice. Brain peptone is hydrolysed only by brain and kidney juices. E. F. A.

Some Conditions Affecting the Activity and Stability of Certain Ferments. JOHN H. LONG and WILLIAM A. JOHNSON (*J. Amer. Chem. Soc.*, 1913, **35**, 1188—1201).—An extension of the earlier investigation on amylopsin (this vol., i, 919) to trypsin. Raw egg-albumin is found to be unsuited to the measurement of proteolytic action, and where egg-albumin is necessary, the authors make use of a Chinese dried albumin; but fibrin and casein are the best materials for comparative studies.

It is found that trypsin is not appreciably injured by the action of 0·3% hydrochloric acid for thirty minutes at 40°, for, although no digestion will occur in the presence of the acid, fibrin can be digested in considerable quantity after neutralisation.

Aqueous solutions of trypsin become weaker on long keeping at the ordinary temperature, the deterioration being more rapid the purer the product; in this respect it is more sensitive than pepsin. In the

presence of sodium carbonate between the concentrations 0·2% and 1% at 40°, the activity of trypsin in fibrin digestion is not affected.

<div align="right">D. F. T.</div>

Purification of Invertase Preparations by Treatment with Acids. JAKOB MEISENHEIMER, STEFAN GAMBARJAN, and L. SEMPER (*Biochem. Zeitsch.*, 1913, **54**, 108—121).—It is found that the content of invertase in a preparation can be increased by preliminary treatment of the expressed juices with acids. Not only acetic, but also hydrochloric, and more especially the dibasic sulphuric and oxalic acids effect this purpose. The addition of acids produces a precipitate of proteins, which carries down with it practically none of the ferment. The addition of too much acid acts deleteriously on the ferment, and for every preparation it is necessary, by means of preliminary experiments, to ascertain the amount of acid which yields the optimal result. For this purpose, the ferment is precipitated by means of acetone, and obtained in a dry form, and its reaction constant is determined polarimetrically with the employment of the equation $K = 1/t \log.a/a—x$. The above-stated facts are illustrated by numerous examples.

<div align="right">S. B. S.</div>

Inhibition of Enzyme Action by Lime-softened Waters. OLAF BERGEIM and PHILIP BOUVIER HAWK (*J. Amer. Chem. Soc.*, 1913, **35**, 1049—1056).—It is found that lime-softened waters exert a pronounced inhibitory effect on the action of salivary and pancreatic amylases. Of the mineral constituents of the water, magnesium hydroxide exerts by far the greatest effect, whilst sodium carbonate and calcium carbonate have a less considerable effect. Investigation shows that the influence of the magnesium hydroxide is due to its existence in a colloidal form which adsorbs the enzyme. In contrast to the action of amylolytic ferments, peptic digestion is but little affected by magnesium hydroxide solution or by lime-softened water.

From the difference in effect of calcium carbonate solution on salivary amylase and pancreatic amylase, it appears that these enzymes are not identical.

<div align="right">D. F. T.</div>

Action of Ammonia on Diastase Rendered Inactive by Heating. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **86**, 401—406).—Ammonia gas has the same effect on diastase whether it has been rendered inactive by heating or not. It cannot therefore have any action on those groupings in the molecule which are altered by heat, that is, on the groupings to which the activity of the enzyme is due.

<div align="right">E. F. A.</div>

Action of Hydrogen Chloride and Ammonia on Diastase Rendered Inactive by Heating. XI. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **87**, 115—121).—Diastase which has been rendered inactive by heating, regains some feeble activity when treated first with dry hydrogen chloride and then with dry ammonia.

<div align="right">E. F. A.</div>

The Enzymes of the Tobacco Plant. J. DU P. OOSTHUIZEN and OLIVER MARCH SHEDD (*J. Amer. Chem. Soc.*, 1913, **35**, 1289—1309). —An investigation of the enzymes in two types of Kentucky tobacco, the White Burley variety of the Burley region, and the Yellow Pryor variety of Western Kentucky.

The results indicate the presence of appreciable amounts of invertase, diastase, emulsin, and reductases both in the seed and in the leaf at all stages of its growth and after curing. Small amounts of lipase, inulase, and a proteolytic enzyme also appear to be present. Oxydases were present in the green leaf, but the quantity decreased towards maturity, and was too small for definite detection in the cured leaf. Generally enzymes were found to be absent from the soil.

The probable rôles of the various enzymes are discussed.

D. F. T.

Enzymes in the Leaves of Salix caprea. IWAN BOLIN (*Zeitsch. physiol. Chem.*, 1913, **87**, 182—187. Compare Armstrong, A., 1912, i, 816).—The leaves of *Salix caprea* may contain a salicase, an amygdalin-splitting and a glucoside-splitting enzyme. Salicase is specific for salicin, and has no action on β-methylglucoside. The enzyme acting on β-methylglucoside was present in the leaves in 1911, but absent from the leaves of the same tree in 1912.   E. F. A.

Enzyme Action. XXI. Lipase. III. HENRY E. ARMSTRONG and H. W. GOSNEY (*Proc. Roy. Soc.*, 1913, *B*, **86**, 586—600. Compare A., 1906, i, 126; 1907, i, 103; Tanaka, A., 1910, i, 800).—Methods of preparing active lipase preparations from castor oil seeds in the form of a dry powder and of testing their hydrolytic activity are described. Dilute acetic acid is used to activate the zymogen, which is probably a salt. Lipase is very sensitive to the action of acids, and easily rendered inert by excess of acid. The inferiority as a hydrolyst of esters other than fats is due to the fact that the acids liberated from fats are scarcely soluble in water and very weak.

Lipase is specially fitted to hydrolyse the oily glycerides, and is not suited to act in aqueous solutions. Interaction takes place at and between surfaces separated only by a thin film of water. The inter-action of enzyme and oil is inhibited by both the fatty acid and the glycerol, especially the former. As in other cases of enzyme action, the law of mass action does not apply, and the influence of the products of change and the destruction of the enzyme combine to cause departures from the simple law of enzyme action (compare this vol., i, 116).

Lipase is considered to contain a glycerol nucleus attached to a carboxylic centre in proximity to an acidic group, which can determine the hydrolysis of a fatty molecule that becomes attached to the glycerol acceptor.   E. F. A.

Some New Properties of Peroxydase. The Comparison of its Action with that of Nitrites. JULES WOLFF (*Ann. Inst. Pasteur*, 1913, **27**, 554—567. Compare A., 1912, i, 928).—Plant sap is sufficiently acid to liberate nitrous acid from nitrites. The nitrous

acid thus set free is able to bring about oxidation phenomena similar to those caused by the combination of a peroxydase with hydrogen peroxide. Nitrites are decomposed by monopotassium phosphate.

Peroxydase can be kept for some time in contact with ammonia without being changed. At first the oxidising activity diminishes somewhat, but then it increases, reaching the original value in four to five hours and attaining a maximum activity in forty hours, nearly double the original. This high activity persists for a time and then decreases slowly to the original value.

Orcinol absorbs oxygen from the air in presence of alkali hydroxides, carbonates, etc. The rate of absorption is greatly increased on adding a vegetable peroxydase—it may amount to five times the original value.

When the surface exposed to the air is large, orcinol absorbs oxygen, but does not form any quantity of coloured oxidation product (orcein). The addition of peroxydase increases the oxygen absorption, but not the amount of colour formed. On the contrary when the surface exposed to the air is small, only about one-seventh of the amount of oxygen is absorbed, but orcein is formed. Peroxydase accelerates the formation of the orcein and not the absorption of oxygen under these conditions.

E. F. A.

Preparation of a Nitro-3-aminophenyl-1-arsinic Acid. FARB WERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 261643. Compare Bertheim, A., 1911, i, 1055).—When *3-oxalylaminophenyl*-1-*arsinic acid*, $C_6H_4(AsO_3H_2)\cdot NH\cdot CO\cdot CO_2H$, needles, is dissolved in sulphuric acid, treated at 0—5° with 26% nitric acid, and the oxalyl group subsequently eliminated, it gives rise to the hitherto undescribed 6-*nitro-3-aminophenyl-*1-*arsinic acid*, pale yellow needles; this when heated with concentrated alkalis yields 6-nitro-3-hydroxyphenylarsinic acid, whilst the mother liquor furnishes 2-nitro-3-aminophenylarsinic acid; and on reduction with sodium hyposulphite the corresponding diaminodihydroxyarsenobenzenes are obtained.

F. M. G. M.

Preparation of Neutral Derivatives of 3:3'-Diamino-4:4'-dihydroxyarsenobenzene, Soluble in Water. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 260235).—The preparation of compounds by the action of formaldehyde sulphoxylate on 3:3'-diamino-4:4'-dihydroxyarsenobenzene have previously been described (A., 1912, i, 595), and the reaction has now been modified by dissolving the hydroxy-base in ethylene glycol before treating with formaldehyde sulphoxylate and subsequently isolating the product by the addition of alcohol and ether.
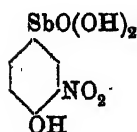
F. M. G. M.

Preparation of Aromatic Stibinic Acids. CHEMISCHE FABRIK VON F. HEYDEN (D.R.-P. 261825. Compare this vol., i, 416).—p-*Chlorophenylstibinic acid*, a colourless powder, is obtained when a solution of *p*-chlorobenzenediazonium chloride is treated with antimony trichloride and the yellow precipitate of the additive compound (compare
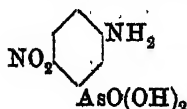
May, T., 1912, **101**, 1037) collected and decomposed with warm sodium hydroxide; it is purified by methods previously described (*loc. cit.*).

Phenylstibinic acid can also be obtained when aniline is diazotised in the presence of a mixture of antimony trichloride and hydrochloric acid, and the cooled solution slowly added to a solution of sodium hydroxide, when elimination of nitrogen occurs with the formation of the required product.   F. M. G. M.

Preparation of an Aromatic Nitrohydroxystibinic Acid.
CHEMISCHE FABRIK VON F. HEYDEN (D.R.-P. 259875. Compare A. 1886, 884; 1899, i, 209; 1910, i, 803; 1911, i, 594, 1056).—*3-Nitro-4-hydroxyphenylstibinic acid* (annexed formula) is prepared by the following series of reactions. Anhydrous sodium *p*-acetylaminophenylstibinic acid (this vol., i, 416) dissolved in acetic acid (3 parts) is added drop by drop to 8 parts of concentrated sulphuric acid at a temperature below −2°; above this, elimination of the acetyl group occurs; nitric acid (D 1·51) mixed with concentrated sulphuric acid at 0° is then added, and the mixture maintained at this temperature for several hours with continual agitation; on dilution, *3-nitro-4-acetylaminophenyl-1-stibinic* acid is obtained as a yellowish-brown powder; this when heated with a solution of potassium hydroxide (D 1·30) loses ammonia and gives rise to the foregoing 3-nitro-4-hydroxyphenyl-1-stibinic acid, a brown powder, which when heated decomposes without fusion.

SbO(OH)$_2$

NO$_2$

OH

                                                                F. M. G. M.

Physiological Chemistry.

A Respiration Apparatus for Small Animals in which the Oxygen Consumption is Automatically Registered. L. S. FRIDERICIA (*Biochem. Zeitsch.*, 1913, **54**, 92—167).—This apparatus combines the Haldane principle, according to which the animal with all excreta are weighed before and after the experiment, the water and carbon dioxide given out by the animal being collected in the ordinary absorption apparatus, with the Regnault-Reiset principle, modified more or less according to Benedict, in which the oxygen which is used up in respiration is automatically replaced from a gasometer, the amount added to the respiration apparatus being automatically registered. For these purposes a circulation is kept up through a closed system by means of a specially designed rotatory blower, which is figured in the text, and the air after leaving the cage containing the animal passes over weighed sulphuric acid and soda-lime tubes. In conjunction with this system is the oxygen holder, the lid of which is counterpoised by a

weight over a pulley, and the whole circuit is so arranged, by the interposition of wash-bottles serving as manometers, that it is constantly under atmospheric pressure. There is a double check, therefore, on the oxygen consumption, namely, the diminution of the oxygen in the gasometer, which is automatically registered, and the gain of weight in the animal holder and absorption apparatus. Both determinations yielded results concordant with one another.

S. B. S.

The Part Played by the Lungs in the Oxidative Processes of the Body. C. LOVATT EVANS and ERNEST H. STARLING (*J. Physiol.*, 1913, **46**, 413—434).—The gaseous metabolism of the lung in the perfused heart-lung preparation is best measured in reference to the heart-weight as the lungs soon become œdematous. It is 1 c.c. of oxygen and 0·94 c.c. carbon dioxide per gram of heart per hour. The lungs do not exercise any general or specific activity in completing oxidations partly carried out in other tissues. W. D. H.

The Influence of the Carbon Dioxide Tension of the Blood on the Ventilation by the Lungs. OTTO PORGES and A. L. SAMPLE (*Biochem. Zeitsch.*, 1913, **54**, 182—185).—In investigations on the influence of the acidity of the blood on the respiration, many authors have attempted to ascertain the stimulability of the breathing centre. Lindhard, more especially, has determined this factor, by allowing the subject of the research to inhale ordinary atmospheric air, and estimating the alveolar ventilation and carbon dioxide tension, and then determining the same factors after inhalation of air to which has been added varying amounts of carbon dioxide. Attention is now called to the fact that in these and similar experiments no account is taken of the fact that the effect on inhaling increased amounts of carbon dioxide will vary according to the pre-existing stimulus. As this pre-existing stimulus depends on the acidity of the blood, it is necessary to take into account, not only the carbon dioxide tension, but also the amount of non-volatile acids, which, according to Porges and his co-workers, are present accompanied by a diminished carbon dioxide tension in acidosis. The influence of the amounts of acid on the action of lungs is illustrated by some experiments on a pregnant patient, and patients with diabetes, and the conclusion is drawn that the method employed by Lindhard and others is not adapted to the determination of the true stimulability of the respiratory centre. S. B. S.

Influence of Alcohol on the Respiratory Exchange During Rest and During Muscular Exercise. C. J. C. VAN HOOGENHUYZE and J. NIEUWENHUYSE (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 164—172).—The authors have subjected themselves to experiments on the influence of alcohol on the respiratory exchange. While resting, they measured the oxygen-intake and carbon dioxide-output by means of the Zuntz-Geppert apparatus, and found that the respiratory quotient, CO_2/O_2, remained lower for a few hours after

the consumption of alcohol. The experiments involving muscular exercise were performed on a bicycle with adjustable and registrable resistance. The brake-band was tightened until the subject was fatigued, and then, whilst he was pedalling against a constant resistance, without or after a dose of 60 c.c. of 96% alcohol, the respiratory exchange was examined as above. The experiments were performed at 8—15° and at 28°. The respiratory quotient was again found to be lowered for a time after the consumption of alcohol, even at the higher temperature, at which muscular work was less economically performed. Alcohol, therefore, can produce energy for muscular exercise, and this is more economically performed for an hour or two after taking the stimulant. This favourable influence, however, gradually decreases, and tends towards the opposite in time.   J. C. W.

The Influence of Muscular Rigidity on the Oxygen-intake in Decerebrate Cats. HERBERT E. ROAF (*Quart. J. expt. Physiol.*, 1913, **6**, 393—402).—During decerebrate rigidity the oxygen intake is only slightly greater than when the muscles are flaccid.
                                                                    W. D. H.

Rate of Reproduction of the Blood Constituents in an Immunised Horse After a Large Bleeding. R. A. O'BRIEN (*J. Path. Bact.*, 1913, **18**, 89—98).—After the withdrawal of ten litres of blood from an immunised horse, the fluid first appearing in the circulatory system contains an amount of protein far above the normal; hæmolysin and diphtheria antitoxin are reproduced at different rates, and the rate of reproduction of the various blood-proteins is probably associated therewith. Details regarding salts and corpuscles are also given.   W. D. H.

The Effect of Certain Drugs, Toxic Substances, and Micro-organisms on the Fragility of the Red Corpuscles of Man and Animals. W. W. C. TOPLEY (*J. Hygiene*, 1913, **13**, 191—236).—Arsenious acid and atoxyl in toxic doses increase the fragility of red corpuscles *in vivo*. Bile and bile salts cause no change. Various pathogenic hæmolytic micro-organisms cause a rise in fragility, so also do specific hæmolytic sera; the amboceptor alone does not. Experiments *in vitro* were not satisfactory, but, so far as they went, the results confirmed the findings *in vivo*.   W. D. H.

The Formation of Indophenol at the Nuclear and Plasma Membranes of Frog's Blood Corpuscles, and its Acceleration by Induction Shocks. RALPH S. LILLIE (*J. Biol. Chem.*, 1913, **15**, 237—247).—The formation of indophenol by the intracellular oxidation of α-naphthol and dimethyl-p-phenylenediamine takes place most rapidly in the neighbourhood of the nuclear and plasma membranes. This is accelerated by passing induction shocks through the suspension of blood corpuscles.   W. D. H.

Rapid Method of Preparing Thrombin. WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1913, **32**, 264—265).—Pig's fibrin is well washed,

and then extracted with 8% solution of sodium chloride; the extract is heated with an equal volume of acetone; the bulky precipitate of protein contains thrombin; this is filtered off and rapidly dried, then extracted with water, and filtered; the filtrate contains the thrombin, traces of salt, and a heat-coagulable protein; the latter is removed by shaking with chloroform, and the final fluid is evaporated to dryness in a current of cold air. The dried material can be left indefinitely in a desiccator. It is easily and completely soluble in water. W. D. H.

The Relation of Metathrombin to Thrombin. F. W. WEYMOUTH (*Amer. J. Physiol.*, 1913, **32**, 266—285).—The thrombin content of serum is determined by its clotting power on solutions of fibrinogen, and the metathrombin content by the clotting power after activation by alkali and subsequent neutralisation. In dog's serum the activity of both disappears after three to four days; five to eighteen days later there is almost complete return, and then it disappears completely. If kept sterile the initial loss of power is slower, and there is no reappearance of activity. Bacterial growth is responsible for both phases. Thrombin prepared by Howell's method retains its power for long periods (at least eighteen days); its power is destroyed by a substance in serum and in oxalate plasma, which is antithrombin. After the action of antithrombin the presence of metathrombin can still be shown in certain cases. Metathrombin is regarded as a thrombin-antithrombin compound; it is absent in oxalate and fluoride plasma. W. D. H.

The Nitrogen of Blood-serum Freed from Protein. RUDOLF PHILIPP (*Zeitsch. physiol. Chem.*, 1913, **86**, 494—502).—The residual nitrogen after serum has been freed from protein by heat-coagulation is about twice as great as when phosphotungstic acid, uranyl acetate, or ferrum oxydatum dialysatum are employed. The two last-named reagents entirely free the serum from protein. In cases of uræmia the residual nitrogen is increased. W. D. H.

Alterations Produced in Complement-containing Sera by the Introduction of "Lecithin." JOHN CRUICKSHANK and THOMAS J. MACKIE (*J. Path. Bact.*, 1913, **18**, 99—113).—"Lecithins" differ markedly with regard to their power to produce the alterations in complement activity, hæmolysis, etc., with which the paper deals. A large number of preparations are quite inefficient. W. D. H.

Fibrin in Sol and Gel State. The Blood-coagulation Problem. EBEL HEKMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 172—185).—The author has investigated the relation between fibrinogen and fibrin. Pure fibrin, free from blood corpuscles, was found to dissolve quite readily in very dilute sodium hydroxide or sodium carbonate, but a fibrous coagulum could be reproduced by the cautious addition of dilute acids, such as phosphoric or carbonic, or by sodium dihydrogen phosphate or calcium chloride.

Fibrin also dissolved in a slight excess of acid, but could be repre-
cipitated on neutralisation. Coagulation was also effected. in
solutions which had been boiled, from which the conclusion is
drawn that ferments play no part in the process. Fibrin is there-
fore a reversible gel.

Further experiments showed that centrifugated, fluid plasma, or
ascites fluid (that is, a natural fibrinogen solution), like alkaline
fibrin solutions, could be coagulated by traces of acids. Moreover,
alkaline fibrin solutions could be coagulated by serums or organic
extracts which are known to coagulate fibrinogen, and also, like
fluid plasma or ascites fluid, by means of saturated solutions of
sodium chloride or fluoride. A great similarity was thus estab-
lished between fibrinogen as found in blood and body fluids, and a
solution of fibrin in very dilute alkali.

Dried fibrils, the single threads of fibrin, swell out again very
quickly in alkaline solutions, and, if the volume of liquid is small,
raw fibrin will imbibe the whole of it and become jelly-like. A
swollen fibril, however, contracts to its original size in dilute acids,
1% calcium chloride or any saturated salt solution, or even in
excess of water. The swelling process is therefore of a superficial
kind, and it is assumed that it consists in the formation of an
alkali adsorption-compound, which eventually, by the continuation
of the imbibition, passes into colloidal solution. Fibrinogen is thus
considered to be an alkali-hydrosol of fibrin, and its conversion into
the gel, fibrin, and therefore the coagulation of blood, is merely due
to the withdrawal of hydroxyl ions from the adsorption compound
by means of one or other of the factors mentioned above.

<div style="text-align:right">J. C. W.</div>

The Inhibition of Hæmolysis by Cholesterol and Oxy-
cholesterol. E. SCHREIBER and LÉNARD (*Biochem. Zeitsch.*, 1913,
54, 291—296).—A method is described for preparing oxychole-
sterol from cholesterol, and of obtaining emulsions of the same.
Although, by itself, the former substance has a much weaker
power of inhibiting hæmolysis than cholesterol, it increases this
power of the latter substance when added to it in quite small
quantities. Oxycholesterol acts also more weakly than cholesterol
in inhibiting hæmolysis by cobra poison. S. B. S.

· The Influence of Nutrition on the Gaseous Metabolism of
Cold-blooded Animals. BERNHARD ELSAS (*Zeitsch. Biol.*, 1913, **62**,
1—31).—The experiments were made on groups of frogs in a
modified Regnault-Reiset apparatus. The inanition metabolism is
first found; but as this is influenced by the temperature, all the
observations must be carried out at a constant temperature. Food
may then be given in amounts equivalent to the inanition meta-
bolism (isopeinic), or the quantities may be below or above this
(hypo- and hyper-peinic respectively). Iso- and hyper-peinic
administration of dextrose increases the metabolism by from 6 to
20%. Isopeinic feeding with fat does not raise the metabolism.
The increase of metabolism after isopeinic feeding on protein is

very pronounced, 17—40%. These results are compared with some previously published by Weiss. The observations lend no support to the view that the increase of activity is due to alimentary work, but confirm Rubner's views on the specific dynamic values of foods.

W. D. H.

Metabolism of Ammonium Salts. I. The Estimation of Ingested Ammonium Salts in the Dog on an Adequate Mixed Diet. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1913, 15, 321—335).—Ammonium salts of organic acids were given to dogs on a fixed diet, but failed to increase the ammonia nitrogen of the urine. Ammonium salts and inorganic acids caused a varying degree of increase in the ammonia nitrogen of the urine. The experiments afford no adequate explanation for the temporary retention of the ammonium salts. All the inorganic ammonium salts used, and some of the organic salts, cause a distinct excess of total urinary nitrogen, and they apparently stimulate nitrogenous katabolism. Sodium chloride under the same conditions lowers the output of urinary ammonia nitrogen.

W. D. H.

Metabolism of Ammonium Salts. II. Elimination of Ammonium Salts During a Period of Prolonged Inanition. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1913, 15, 337—339).— During inanition in the dog, ingestion of ammonium carbonate fails to produce an increase of urinary ammonia nitrogen. Ammonium chloride causes, however, a marked increase, and also an increase in total nitrogen. At this stage a second ingestion of ammonium carbonate may also bring about an increase of total urinary nitrogen.

W. D. H.

Metabolism of Ammonium Salts. III. The Utilisation of Ammonium Salts with a Non-nitrogenous Diet. FRANK P. UNDERHILL and SAMUEL GOLDSCHMIDT (*J. Biol. Chem.*, 1913, 15, 341—355).—Ammonium chloride added to a non-nitrogenous diet caused no retention of nitrogen, as Grafe states. It exercises a toxic action, and increases the output of urinary ammonia. Ammonium acetate and citrate decrease the nitrogen loss, and lead to retention of nitrogen. The ability of the body to deal with the organic and inorganic salts of ammonium is radically different. W. D. H.

Excretion of Creatine. R. A. KRAUSE (*Quart. J. expt. Physiol.*, 1913, 7, 87—101).—The metabolism of children differs from that of the adult. In boys, creatinuria occurs until the age of five or six; in girls it persists longer, and may last until the intermittent creatinuria occurs which characterises the female sexual cycle. The power to assimilate creatine given with the food is much weaker in children than in the adult. The excretion or non-excretion of creatine depends on the balance between formation and destruction, two processes which are always at work. This view will render it necessary to revise current theories on creatinuria as a pathological condition. W. D. H.

Nitrogen Retention in Feeding on Urea. EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, 86, 347—355).—These experiments are given to support the author's contention (compare A., 1912, ii, 659; 1913, i, 216) that urea in the food leads to retention of nitrogen. The experiments lasted over a long period. W. D. H.

The Relation of Growth to the Chemical Constituents of the Diet. THOMAS B. OSBORNE, LAFAYETTE B. MENDELL, EDNA L. FERRY and ALFRED J. WAKEMANN (*J. Biol. Chem.*, 1913, 15, 311—326).—It has been previously shown that growth and mainten-ance are different things. The best food to promote growth is milk, even if only small quantities are occasionally given, mixed with an artificial diet of protein, fat, carbohydrates, and salts. Protein-free milk is not adequate for growth, but the addition of butter to the protein-free milk restores growth. Evidently some substance is removed from the protein-free milk which is essential, and this is present mixed with the butter-fats. What the substance is, is as yet unknown.   W. D. H.

Sugar Absorption. KORNÉL VON KÖRÖSY (*Zeitsch. physiol. Chem.*, 1913, 86, 356—367).—By interference with the circulation through the intestines, lungs, and heart, absorbed sugar does not occur as such in the blood. The absorption of sugar is not a simple process, and the effect of internal secretions, such as that of the adrenal gland, has to be taken into account. Phosphates may also play an imporant rôle in sugar absorption, as they do in alcoholic fermentation.   W. D. H.

The Distribution of Creatine in the Animal Organism J. C. BEKER (*Zeitsch. physiol. Chem.*, 1913, 87, 21—37).—A large number of organs and tissues in different animals were found to contain creatine in amounts which are greater than that in the blood. These results are given in tables. Experiments are also given which confirm the view that the liver is able to convert creatine into creatinine.   W. D. H.

The Lecithin Content of Different Tissues. JOHN CRUICKSHANK (*J. Path. Bact.*, 1913, 134—136).—The amount of lecithin in various tissues was estimated by the author's method. In 100 grams of moist tissue, ox red corpuscles yielded 2·5, sheep's liver 1·6, human brain 0·6, ox pancreas 0·68, testicles 0·62 gram, and other tissues amounts varying from 0·14 to 0·48 gram.   W. D. H.

Gases Evolved During the Autolysis of Some Organs and Tissues. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, 43, ii, 144—148). —The liver, kidney, brain, and suprarenal capsules yield carbon dioxide, nitrogen, and hydrogen; the intestine evolves carbon monoxide and oxygen in addition to these gases, whilst the pancreas, spleen, lungs, and heart yield only nitrogen. R. V. S.

Calcium and Magnesium in the Brain Under Different Physiological and Pharmacological Conditions. IVO NOVI (*Eighth Inter. Cong. App. Chem.*, 1912, 19, 261).—The proportion of

calcium in the brain of the dog varies from 0·0143 to 0·031, and that of magnesium from 0·0143 to 0·0167% of the fresh material. Age has a marked influence on the calcium-content of the brain. With dogs this content is at its maximum before and just after birth, the minimum is reached prior to weaning, and in old age the initial value is again attained; a similar course is followed in the case of the human brain. With guinea-pigs, the proportion of calcium is minimal in the fœtus, becomes almost doubled a few days after birth, and continues to increase for a month; subsequently it remains constant until old age is reached, when it again increases, sometimes as much as tenfold. Introduction, either subcutaneously or into the stomach, veins, or carotids, of sodium chloride in isotonic or hypertonic solution results in the diminution of the calcium-content of the brain, in some cases by one-half.

The proportion of magnesium in the brain remains constant at all ages and under all the experimental conditions employed.

T. H. P.

Cerebrosides of Brain Tissue. ⁞PHOEBUS A. LEVENE (*J. Biol. Chem.*, 1913, 15, 359—364).—The conclusion that the cerebrosides are optically different isomerides is confirmed by further work, but more data are still wanting to render this certain. W. D. H.

Autolysis of, and Presence of, Proteolytic Ferments in the Brain of the Calf. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, 43, ii, 138—143).—When the brain of the calf is subjected to autolysis (incubation with water in presence of chloroform for a month), lysine, choline, xanthine, and adenine can be subsequently obtained from it. This indicates the presence in the brain of ferments capable of attacking albumin, nucleins, and lecithin. R. V. S.

The Effect of Alcohol on the Excitation, Conduction, and Recovery Processes in Nerves. KEITH LUCAS (*J. Physiol.*, 1913, 46, 470—505).—After exposure to 5% alcohol, a nerve recovers its properties when replaced in Ringer's solution. The impairment of conduction in the nerve produced by alcohol, and the increase in threshold current strength follow a parallel course. The rate of conduction is much slowed, however, at a stage when the rate of recovery is not slowed. This suggests that the recovery process, which is responsible for the refractory period, is a process different from the disturbance which is the basis of propagation of the nervous impulse. W. D. H.

The Influence of Anoxybiosis on the Disappearance of Glycogen from the Autonomous Organs of the Frog. ERNST J. LESSER (*Biochem. Zeitsch.*, 1913, 54, 236—251).—As autonomous organs are designated those tissues, such as liver and muscles, in which action takes place when they are separated from the nervous systems, and the hormones contained in the blood supply. The author has already shown that the rate of glycogen disappearance from the liver after removal from the animal is greater in summer

frogs than in winter frogs, and he now compares this rate when the organs are well supplied with oxygen (oxybiosis) and when they are kept in a current of nitrogen (anoxybiosis). These experiments were of interest, as it has been found that under the influence of anoxybiosis of the whole animal the rate of glycogen disappearance could be increased, and it was thought possible that by this means the behaviour of the livers from winter frogs could be made to approximate to that of summer frogs. It was found that in the months of the year in which the glycogen of the liver is stable, the rate of disappearance is not influenced by anoxybiosis, whereas in the months when the glycogen is labile, anoxybiosis increases the rate. The experiments were carried out at the temperature of 22—24°, and did not extend beyond five hours. Similar results were obtained with muscular tissues.   S. B. S.

Chemical and Bio-chemical Properties of the Lipoids Extracted from Pig's Liver and Egg-yolk. FREDERICK P. WILSON (*J. Path. Bact.*, 1913, **18**, 60—63).—The lipoids extracted from pig's liver and from egg-yolk differ greatly in their chemical (iodine value, etc.) and biochemical (anti-complementary, hæmolytic powers, etc.) properties.   W. D. H.

The Thyroid Gland. XI. WALTER EDMUNDS (*J. Path. Bact.*, 1913, **18**, 52—59).—The thyroid gland in dogs hinders the assimilation of sugar; the parathyroid glands favour it.   W. D. H.

Carbohydrate Metabolism in its Relation to the Thyroid Gland. The Effect of Thyroid Feeding on the Glycogen-content of the Liver and on the Nitrogen Distribution in the Urine. W. CRAMER and R. A. KRAUSE (*Proc. Roy. Soc.*, 1913, *B*, **86**, 550—560).—When rats or cats are fed on a carbohydrate-rich diet plus small amounts of fresh thyroid gland for two or three days, the liver only contains traces of glycogen. This is due to an inhibition of the glycogenic function of the liver, and not to increased utilisation of carbohydrates. There is no glycosuria. The distribution of the nitrogenous constituents in the urine is similar to that observed after withdrawal of carbohydrates from the diet.   W. D. H.

Changes in the Metabolism of Animals After Extirpation of the Thyroids and Parathyroids. J. GREENWALD (*Biochem. Zeitsch.*, 1913, **54**, 159—160).—The author controverts the statement of Paladino (this vol., i, 675) that there is an increased phosphorus output after extirpation of the thyroids. He contends that there is rather a diminution, and the discrepancy between Paladino's results and those of other authors is due to the fact that the former did not investigate the metabolism immediately after the operation, but only after a prolonged period at the onset of tetany, which, it is admitted, may produce increased phosphorus output.   S. B. S.

The Enzymes of the Pituitary Body. LUCIE BUETOW (*Biochem. Zeitsch.*, 1913, **54**, 40—52).—The following ferments were found to be present: Catalase, diastase, pepsin, trypsin, peroxydase, tributyrinase, and urease. The following enzymes could not be detected: Invertase, lactase, a glycolytic ferment, and deamidase. S. B. S.

The Chemistry of the Mammary Gland. J. ARGYLL CAMPBELL (*Quart. J. expt. Physiol.*, 1913, **7**, 53—56).—Considerable differences exist in the mammary gland of different animals, and even between different parts of the gland in the same animal. Lactose is found only when the gland contains milk, and the amount present is thus a measure of the quantity of milk in the gland. The fat, on the other hand, is present, not only in milk, but in the secreting cells, and in the adipose tissue between the alveoli. W. D. H.

The Phosphatides of Human Placenta. III. C. SAKAKI (*Biochem. Zeitsch.*, 1913, **54**, 1—4).—From the alcohol-ether obtained in the purification of the so-called jecorin by Drechsel's method, a precipitate was obtained on addition of alcoholic cadmium chloride, part of which was soluble in ether and the other part insoluble. Both these products were analysed, but the results do not accord with any definite chemical formula. S. B. S.

The Distribution of Phosphorus in the Placenta. C. SAKAKI (*Biochem. Zeitsch.*, 1913, **54**, 5—10).—From the determination of the phosphorus soluble in organic solvents (light petroleum or benzene) the amount of lecithin was calculated as 6·8% of the dried substance. S. B. S.

The Absorption of Water by the Skin of the Frog. S. S. MAXWELL (*Amer. J. Physiol.*, 1913, **32**, 286—294).—An empty frog's skin immersed in water takes up an enormous amount; this depends on the permeability of the skin to water, and its relative impermeability to salts. The assumption of "vital activity" in this process is regarded as unnecessary. W. D. H.

The Absolute Mechanical Efficiency of the Contraction of an Isolated Muscle. ARCHIBALD V. HILL (*J. Physiol.*, 1913, **46**, 435—469).—Fick's results on the mechanical efficiency of muscular contraction are inaccurate; for instance, they do not take into account the heat-production which occurs in the period of recovery. The subject was re-investigated by the author's new methods; his apparatus, however, requires calibration for each experiment and each muscle used. In the sartorius, the initial process of contraction consists mainly of the liberation of free potential energy, which is manifested as tension energy in the excited muscle; this can be used indifferently for the production of work or of heat; the efficiency of the whole process may be almost as high as 50%. The chemical substance possessing the free energy is the lactic acid precursor. W. D. H.

Extractives of Muscle. XV. Presence of Carnosine, Methyl-guanidine, and Carnitine in Horse Flesh. J. SMORODINZEV (*Zeitsch. physiol. Chem.*, 1913, **87**, 12—20).—Horse flesh is shown to contain about 0·58 gram of creatine, 0·08 gram of purine substances, 1·82 gram of carnosine, 0·18 gram of carnitine, and from 0·11 to 0·83 gram of methylguanidine per kilogram of fresh muscle. These proportions are those observed in the muscles of other animals. E. F. A.

The Influence of Starvation on the Creatine Content of Muscle. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1913, **15**, 283—304).—The creatine of rabbit's muscle is relatively increased in the early part of starvation, but decreased at the close, owing to its loss by the urine. That creatine and creatinine are independent in metabolism is dissented from; the old view that the creatinine is derived from muscular creatine is favoured, though the proof is not yet complete. W. D. H.

Influence of Carbohydrate Feeding on the Creatine Content of Muscle. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1913, **15**, 305—310).—The effect of carbohydrate feeding on the creatine of rabbit's muscles is similar to that seen in starvation. The decreased elimination of creatine under these conditions is primarily dependent on the sparing action of carbohydrate on the muscle proteins. W. D. H.

The Derivatives of Ethyl Alcohol Contained in Muscle. ALONZO L. TAYLOR (*J. Biol. Chem.*, 1913, **15**, 217—220).—In dogs which had been without food for one day, and in which the entire alimentary canal had been extirpated, the muscles still yielded alcohol in small amounts. It could not have been derived from food, and the theory is advanced that alcohol is an intermediate stage in the metabolism of dextrose. W. D. H.

Chemical and Physico-chemical Properties of Liquids Expressed from Striated and Plain Muscle. II. Amount of Protein in the Juice and Relations between the Granules (Myosin) Suspended and the Myoprotein Dissolved. FILIPPO BOTTAZZI and G. QUAGLIARIELLO (*Atti R. Accad. Lincei.*, 1913, [v], **22**, ii, 52—59. Compare Bottazzi, A, 1912, ii, 1192).—The granular substance amounts to 33—61% of the total protein of the juice. The total protein amounts to 5·32—9·54%. Data regarding the yield, density, viscosity, total nitrogen, and ash of the juice obtained in different experiments and with muscle from different animals are also recorded. R. V. S.

Presence of Succinic Acid in Meat Extract and in Fresh Meats. HANS EINBECK (*Zeitsch. physiol. Chem.*, 1913, **87**, 145—158).—Succinic acid in some quantity is obtained, both from Liebig's meat extract and from fresh ox and dog flesh. It is present in the carniferrin fraction, and particularly in the mother liquors from

this. It is not derived from the decomposition of Siegfried's phosphorcarnic acid. E. F. A.

Does Milk Contain Phosphatides? VLADIMIR NJEGORAN (*Biochem. Zeitsch.*, 1913, **54**, 78—82).—Milk was treated with anhydrous sodium sulphate, and the mixture was kept in a vacuum until free from water. The residual powder was then extracted with various organic solvents. No phosphorus could be detected in these solutions, and the author draws the conclusion that phosphatides are not present in milk. S. B. S.

The Effect of Pituitary Extract on the Secretion of Milk. JOHN HAMMOND (*Quart. J. expt. Physiol.*, 1913, **6**, 311—338).— Injection of pituitary extract produces an immediate action on the flow of milk, which is followed by a period of decreased flow. The effect, however, is not muscular, nor is it effected through the rise of blood-pressure. . Microscopic evidence points to a direct action on the epithelium cells which set free the milk constituents. The milk formed is rich in fat. The daily yield of milk is only slightly increased as the result of the injection. W. D. H.

Hydrocephalus Fluid. E. SIEBURG (*Zeitsch. physiol. Chem.*, 1913, **86**, 503—510).—An analysis of fluid from a case of hydrocephalus is given. The noteworthy points are: (1) the absence of protein; a faint reaction with Millon's reagent indicates the presence of certain hydrolytic products of protein; and (2) the presence of certain enzymes, namely, diastase, invertase, lipase, and enzymes capable of splitting glucosides and esters. W. D. H.

The Nature of the Depressor Substance in Dog's Urine and Tissues. ALONZO A. TAYLOR and RICHARD M. PEARCE (*J. Biol. Chem.*, 1913, **15**, 213—216).—Attempts to isolate the substance failed. W. D. H.

The Excretion of Formic Acid in Human Urine Under Normal and Pathological Conditions. RUDOLF STEISOWER (*Biochem. Zeitsch.*, 1913, **54**, 189—211).—The formic acid was estimated by distilling urine acidified with phosphoric acid under diminished pressure, collecting the distillate in excess of alkali, and determining the acid in this distillate after concentration by heating with mercuric chloride in the presence of sodium acetate. The mercurous chloride produced by the reduction was weighed. The yield of formic acid thus found is about 90% of the theoretical. Formic acid is found under normal conditions in the urine to the extent of about 13·5 milligrams daily; and the amount is not increased by moderate muscular activity. It does not appear to be influenced by the character of the diet. In many diseases the amount excreted is normal, as in compensated heart affections, carcinoma, gastric ulcer, colelithiasis, constipation, and various febrile conditions. It is increased, however, in uncompensated heart affections, in asphyxia due to work in heart affections in man,

and in animals. It is also increased in diabetes as the result of changes in the fat metabolism. In a single case investigated of muscular dystrophy there was also found an increased output of the acid, due apparently to changes in the muscular metabolism. Reasons are given for supposing that formic acid is a metabolism product of fats, carbohydrates, and proteins.   S. B. S.

Excretion of Formic Acid in Disease. I. GREENWALD and N. W. JANNEY (*Zeitsch. physiol. Chem.*, 1913, **86**, 511—512).—By the use of the method of Dakin, Janney, and Wakeman, it is shown that the excretion of formic acid in the urine is increased in pneumonia, especially during the stage of resolution. Figures are also given in isolated cases of other diseases, but no generalisations are possible from these.   W. D. H.

Substances in Urine Giving Rise to Indigotin. I. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, **87**, 188—206).—The substances in human urine which give rise to indigotin are very unstable. Their amount has greatly diminished in one to three hours, and they have disappeared in three to six hours. The cause of the decomposition is not understood; it is perhaps due to autoxidation. The indigotin-forming substances were obtained by salting-out and extraction with a mixture of ether and alcohol. Even under these conditions they decompose too rapidly for their isolation to be effected. It is considered improbable that they are identical with potassium indoxylsulphate.   E. F. A.

Excretion of Morphine in the Urine. WILHELM RITTER VON KAUFMANN-ASSER (*Biochem. Zeitsch.*, 1913, **54**, 161—173).—The author finds that neither the biological method of Hermann and Straub (action on white mice) nor the chemical method described by van Ryn are suitable for the quantitative estimation of morphine in the urine. He describes a method devised by himself, in which the morphine is finally extracted with chloroform, and estimated by means of iodoeosin. By this method it is found that larger quantities of the alkaloid are excreted by the kidneys than was formerly supposed, the amount eliminated by this channel reaching 39% during a course of constant administration of the drug. Seventy-two hours after the last injection in this series of experiments sufficient alkaloid could be found in the liver, kidneys, and stomach for quantitative estimation.   S. B. S.

The Antagonism Between Adrenaline and Anæsthetics on the Heart. JAMES A. GUNN (*Quart. J. expt. Physiol.*, 1913, **7**, 75—86).—Using the perfusion method on the heart of cat or rabbit it was found that adrenaline can antagonise a concentration of chloroform which enfeebles the beat, but not such a concentration as arrests it. In the case of chloral the antagonism of adrenaline is greater, and the latter drug will set a heart going which is completely arrested by chloral. Adrenaline is also antagonistic to many other substances which weaken cardiac activity. The

rhythmic contractions which adrenaline arouses in a quiescent heart are independent of intrinsic motor ganglia. W. D. H.

Pharmacological Testing of Sulphuric Acid. Esters of Atropine and Scopolamine. PAUL TRENDELENBURG (*Arch. expt. Path. Pharm.*, 1913, **73**, 118—138).—By the esterification of the alcoholic hydroxyl of alkaloids of the atropine group with sulphuric acid, the intramolecular salt formation with the nitrogen of the tropine or scopolamine causes a marked weakening of their affinity for the endings of the vagus nerve. In most cases the stimulating action on the nervous system is increased. The toxicity is not altered as a rule. The esters of the atropine group stimulate the respiratory centre very strongly; this may be useful therapeutically. The scopolamine ester does not possess this property. W. D. H.

Creatine Formation in the Animal Kingdom. Creatine Formation from Betaine and Choline. OTTO RIESER (*Zeitsch. physiol. Chem.*, 1913, **86**, 415—453).—This paper contains a very useful résumé of recent work on the subject. The experiments recorded deal with the effect of the administration of betaine and choline (by mouth or hypodermically) on the amount of creatine in the muscles, and creatinine in the urine. In some cases the material was mixed with surviving muscle. Although in a certain number of cases creatine or creatinine, as the case may be, was increased, the conclusion is drawn that there is no certain proof that betaine or choline leads to creatine formation. W. D. H.

The Fate of Cocaine and Ecgonine in the Organism. SULEIMAN RIFATWACHDANI (*Biochem. Zeitsch.*, 1913, **54**, 83—91).— Cocaine is excreted, after administration to rabbits, in the urine, in amounts which can be quantitatively estimated. For this purpose the urine is extracted by benzene or ether, and the amount of alkaloid thus obtained is estimated by Gordin's method. By long-continued administration of the drug, the amount excreted each day in the urine gradually increases. No destruction of cocaine, when kept in contact with living tissue, could be detected. Ecgonine is also excreted in the urine; for the purposes of detection the urine was evaporated to dryness and treated with methyl alcohol and hydrochloric acid; the alkaloid after conversion into its methyl ester can be extracted by ether. S. B. S.

The Influence of Lecithin on the Action of Drugs. DAVID M. LAVROV (*Biochem. Zeitsch.*, 1913, **54**, 16—26. Compare Hanschmidt, this vol., i, 796).—A summary is given of earlier experiments on the combined action of lecithin and various drugs on frogs, in which it is shown that within certain limits the lecithin diminishes the action of the drug, whereas within higher limits it increases it. In the cases of phosphorus and phenol poisoning, an increase only of the toxic effect was observed. In doses of 0·0015 to 0·003 gram lecithin markedly increases the toxic action of ricin on frogs. Doses of other magnitudes cause a two-fold action. During the first ten

or eleven days they increase the toxic action, but afterwards the ricin effects begin to weaken. The general condition of the animals employed is not without effect.   S. B. S.

Is the Pressor Effect of Pituitrin Due to Adrenal Stimulation ? R. G. HOSKINS and CLAYTON MCPEEK (*Amer. J. Physiol.*, 1913, **32**, 241—244).—The experiments recorded show that the answer to the question is in the negative.   W. D. H.

Pharmacological Notice Concerning Two New Derivatives of Santonin, α- and β-Santonan (α- and β-Tetrahydrosantonin). E. SIEBURG (*Chem. Zeit.*, 1913, **37**, 945—946).—Pharmacological experiments with α- and β-sodium tetrahydrosantonate (Wienhaus and von Oettingen, this vol., i, 474) show that they are not cramp poisons, neither do they act as vermicides. The reduction of the ethylene linking in santonin thus destroys its specific properties.
T. S. P.

p-Hydroxy-β-phenylethylamine, the Poison in the Salivary Gland of Cephalopods. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1913, **87**, 51—58).—p-Hydroxy-β-phenylethylamine is shown to be the only poisonous constituent of the saliva of the octopus. This base, which had previously been obtained by Barger and Dale from ergot (A., 1909, ii, 689), is thus, like adrenaline, the product of metabolism in a gland.   E. F. A.

Chemistry of Vegetable Physiology and Agriculture.

The Resistance of Spores to Heating in Anhydrous Fluids such as Glycerol and Similar Substances. HOWARD BULLOCK (*J. Hygiene*, 1913, **13**, 168—177).—The method at present in use for the sterilisation of glycerol or oil are quite inadequate; the heating of these fluids has no greater effect than the same temperature in the air. To sterilise these fluids, a temperature of 170° for half an hour or 180° for ten to fifteen minutes is necessary.   W. D. H.

Bacterial Metabolism. XI. Estimation of Urea Nitrogen in Cultures of Certain Bacteria. ARTHUR I. KENDALL and ARTHUR W. WALKER (*J. Biol. Chem.*, 1913, **15**, 277—282).—Urea nitrogen estimated by Folin's method is probably not all due to urea. In bacteria the main nitrogenous end-product of metabolism is ammonia. The urea nitrogen in the culture fluid does not alter.   W. D. H.

Bacterial Metabolism. XIII—XXX. ARTHUR I. KENDALL, ALEXANDER A. DAY, and ARTHUR W. WALKER (*J. Amer. Chem. Soc.*, 1913, **85**, 1201—1249).—An investigation of the effect

of utilisable carbohydrate on the metabolism of protein and protein derivatives by bacteria. The media used consisted of a prepared broth containing meat juice and peptone, and a mixture of the same broth with 1% of dextrose. Four flasks of the sugar-free and of the sugar-containing broths were inoculated with the desired organism and incubated at 37°, the progress of the action being followed by examination of the contents of the flasks over a period of nine days. Determinations were made of the free ammonia, the total nitrogen, the acidity resulting on the addition of formaldehyde, and the acidity or alkalinity of the liquid, using alizarin, neutral red, and phenolphthalein as indicators.

Seventeen groups of bacteria were submitted to examination, and the results are tabulated in the original. D. F. T.

Disinfecting Value of Mercuric Oxycyanide and of Mercuric Oxycyanide Containing Mercuric Cyanide. H. KÜHL (*Arch. Pharm.*, 1913, 251, 340—349).—In general, a solution of a poison at extreme dilution promotes the growth of lower vegetable organisms; at a definite, greater concentration of the poison, the multiplication of the organisms is retarded, whilst at still greater concentrations the poison exerts its lethal action. The author has examined the action on *Bacillus coli* of two samples of mercuric oxycyanide, one practically pure (99%), the other containing 33·3% of oxycyanide and 66·6% of mercuric cyanide. At concentrations of 1 in 200,000 to 1 in 400,000 it is found that solutions of both samples approximately double the rate of growth of the bacilli.

The retarding action of the two disinfectants on the growth of organisms is shown in two ways. Milk coagulates when it contains 0·0005% of either of the two samples, but does not do so when the amount of the poison is increased to 0·005%. In the second set of experiments, urine containing 0·01—0·2% of either of the poisons remains unchanged under the conditions in which the urine alone becomes turbid and evolves ammonia.

Experiments on pure cultures of *Staphylococcus pyogenes*, on raw milk, on tuberculous milk, and on the contents of the stomach and of the intestines and on the brains of a decomposed corpse lead to the astonishing result that there is no appreciable difference in the bactericidal value of the two samples under examination. Another series of comparative experiments shows that the disinfecting value of mercuric oxycyanide is almost equalled by that of a mixture of the oxycyanide and sodium chloride containing 33·3% of the latter. A fuller treatment of the subject is promised; at present the author is of opinion that the sodium chloride, as a disinfectant, slightly active accentuates the bactericidal value of the mercuric oxycyanide by promoting the absorption of the latter substance by the protoplasm. C. S.

Biochemical Reactions of Diphtheria-like Organisms. T. G. M. HINE (*J. Path. Bact.*, 1913, 18, 75—80).—The chief point urged is that the diphtheria-like bacilli, *B. diphtheriae*, alone gives acid with dextrose and dextrin, and not with sucrose. W. D. H

The Inhibition of the Cholera-Red Reaction by Certain Nitrite-destroying Organisms, and on the Mutual Inhibition of B. dysenteriæ (Flexner) and V. choleræ when Grown together. W. J. LOGIE (*J. Hygiene*, 1913, **13**, 162—167).—Certain nitrite-destroying organisms when grown along with *V. cholerae* prevent the appearance of the cholera-red reaction. This is not due to the non-formation of nitrite, but to its rapid destruction by the nitrite-destroying organisms. There are, on the other hand, certain nitrite-destroying organisms which fail to prevent the cholera-red reaction. In the case of *B. dysenteriae* the failure to prevent the cholera-red reaction is due to an inhibition of the growth of both organisms when grown together.   W. D. H.

Spore-producing Bacillus lactis fermentens, a Ferment Producing Butylene Glycol from Lactose. RUOT (*Compt. rend.*, 1913, **157**, 297—299).—*Bacillus lactis fermentens* is a very mobile, anaerobic bacillus, which produces spores after three days on gelose at 30°, which resist a temperature of 90° for five minutes, and can be heated at 100° for half a minute without being killed. It ferments dextrose, sucrose, lactose, mannitol, and glycerol, the products from the sugars being carbon dioxide, hydrogen, alcohol, butylene $\beta\gamma$-glycol, acetylmethylcarbinol, and formic and acetic acids, no lactic or succinic acids being found. The fermentation of milk by this bacillus is very rapid, the products being as above.
                                W. G.

Isolation of B. typhosus from Fæces by means of Brilliant-Green. C. H. BROWNING, W. GILMAN, and T. J. MACKIE (*J. Path. Bact.*, 1913, **18**, 146—148).—The method described is based on the observation that brilliant-green exerts a much more marked inhibitory effect on *B. coli* than on *B. typhosus*.   W. D. H.

Bactericidal Action and Chemical Constitution with Special Reference to Basic Benzene Derivatives. C. H. BROWNING and W. GILMAN (*J. Path. Bact.*, 1913, **18**, 144—146).—*Staphylococcus aureus* and *B. anthracis* are more susceptible to basic benzene derivatives than are organisms of the *Coli* group. It is not possible to differentiate generally that gram-positive organisms are susceptible, and gram-negative organisms are not susceptible to crystal-violet. Salts of the heavy metals do not act less powerfully on the coli-typhoid group than on *S. aureus* and *B. anthracis*. Preliminary details are given of the effects of substituting radicles in benzene derivatives on their bactericidal power; and on the effect of serum on bactericidal action.   W. D. H.

Influence of Ozone on Yeast and Bacteria. CARL A. NOWAK (*J. Ind. Eng. Chem.*, 1913, **5**, 668).—Results of experiments with bottom-fermentation yeast showed that ozonisation is not only of value in freeing the yeast from objectionable organisms which are susceptible to the action of ozone to a larger degree than the yeast itself, but also in eliminating the weakened cells and stimulating the fermentative power of the surviving ones.   W. P. S.

Influence of Mineral Salts on Alcoholic Fermentation. Salts of Tin and Bismuth. MARIUS EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1913, **31**, 49—53).—Stannous chloride even in small amounts retards fermentation. Yeast can be acclimatised so as to ferment well in presence of considerably more stannous chloride than will retard fermentation with ordinary yeast; the yeast, however, rapidly degenerates. Stannic chloride is much more toxic than stannous chloride.

With regard to bismuth, the basic nitrate, with which Gimel obtained favourable results, is quite insoluble when washed with hot water. N. H. J. M.

The Enrichment of the Invertase Content of Living Yeasts. JAKOB MEISENHEIMER, STEFAN GAMBARJAN, and L. SEMPER (*Biochem. Zeitsch.*, 1913, **54**, 122—154).—The effect of allowing various yeasts to remain in contact with various sugars on their content in invertase was investigated. It was found that the amount largely increased by this treatment. Large quantities of the organism were allowed to remain for one to two days in sucrose solutions, which were then cooled on ice, and poured off. A portion of the yeast was then removed, the juice expressed and treated with acetone. The invertase reaction constant of this preparation was then determined. The main portion of the yeast was again treated in a similar way, and the reaction constant of a portion also determined; the main bulk was again treated with sugar, and these processes repeated until the yeast was exhausted. During these successive treatments the invertase content increased, although the zymase content diminished. The relative influence of various sugars on the increase of invertase content was also investigated. In the majority of cases, the yeasts were allowed to grow in a Lindner solution, to which was added the various sugars. It was found that in most of the experiments invert sugar and lævulose caused a larger increase in the invertase than dextrose or sucrose. The lævulose was generally more effective than the invert sugar, and the sucrose slightly more effective than dextrose. The results may possibly be explained on the assumption that a lævulose-invertase combination is somewhat more stable than the combination of invertase with other sugars, and the ferment is thereby more efficiently guarded against change during the autolysis of the yeast. S. B. S.

The Dominance of Roquefort Mould in Cheese. CHARLES THOM and JAMES N. CURRIE (*J. Biol. Chem.*, 1913, **15**, 249—258).—The low percentage of oxygen in the open spaces within the cheese accounts for the dominant activity of *Penicillium roqueforte* in Roquefort and similar cheese. Gas analyses from cultures of various kinds of moulds are presented. W. D. H.

Phenomena of Imbibition in the Seeds of Avena sativa. F. PLATE (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 133—140).—From experiments with solutions of potassium, sodium, barium,

and calcium hydroxides, and of hydrochloric, nitric, sulphuric, and phosphoric acids, the author finds that both cation and anion have specific functions in regard to this phenomenon. The solutions accelerate germination, and considerable concentrations do not spoil germination, but even favour it.   R. V. S.

Compounds Obtained from Plant Seeds by the Methods for Extracting Lecithin. IV. Peas, Larch, Rice. , GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, **86**, 407—414).—Peas contain rather over 1% of lecithin. This yielded galactose on acid hydrolysis and colamine when hydrolysed with barium hydroxide.

The lecithin from larch seeds contained about 3·3% of phosphorus, 0·75% of nitrogen, and 4% of galactose.

Rice which had not been deprived of the husk yielded a lecithin compound having the properties of a cerebroside.   E. F. A.

Distribution of Carboxylase in Plants. W. ZALESKI (*Ber. deut. bot. Ges.*, 1913, **31**, 349—353).—Carboxylase was found in various seeds, such as peas, lupines, *Vicia Faba*, wheat, and maize, in etiolated seedlings, and in moulds.

Although anærobic, carboxylase is active in presence of oxygen; and some of these substances decompose pyruvic acid equally well in air and in hydrogen. Some, however, such as ripening pea seeds, fail to decompose pyruvic acid in presence of air, whilst they are very active in a vacuum. The stem points of *Vicia Faba* decompose pyruvic acid in presence of air if previously extracted with methyl alcohol.   N. H. J. M.

Chemical Composition of Cooked Vegetable Foods. KATHARINE I. WILLIAMS (*J. Ind. Eng. Chem.*, 1913, **5**, 653—656).— Analyses of cooked vegetables, cereals, and leguminous seeds, etc., are recorded (compare P., 1903, **19**, 26).   W. P. S.

Chlorophyll Assimilation. K. VON KŐRÖSY (*Zeitsch. physiol. Chem.*, 1913, **86**, 368—383).—In acacia leaves immersed in nutritive fluids the assimilation of starch and sugar was about 10%, but the fat in the leaves was not increased.   W. D. H.

Composition of the Fruit and Seeds of Adansonia digitata. RUSSELL GEORGE PELLY (*J. Soc. Chem. Ind.*, 1913, **32**, 778—779). —The seeds of the baobab tree (*Adansonia digitata*) consist of a very tough husk enclosing a soft, oily kernel, devoid of starch. Analysis gave, in percentages: moisture, 12·1; ash, 3·5; oil, 11·6; protein (total nitrogen multiplied by 6·25), 11·2; fibre, 22·5; carbohydrates (by difference), 39·1. The ash of the kernels contained: potash, 31·0; soda, 7·2; and phosphoric acid, 34·2%. The oil as extracted by light petroleum had D_{15}^{15} 0·915, saponification value, 190·5—191·7, and iodine value (Hübl, seventeen hours), 76·7—77·8. The seeds are free from alkaloids and cyanogenetic glucosides.

The fruit pulp gave: moisture, 15—16%; ash, 4·76—6·10%;

matter soluble in alcohol, 16·7—18·7%. The ash consisted largely of alkali carbonates, and contained: silica, 4·74; lime, 8·88; potash, 48·90; soda, 4·20; and phosphoric acid, 1·08%. The pulp consisted largely of pectous matter. The free acid extracted by 95% alcohol was found to be citric acid; no indications of tartaric acid were obtained, but small amounts of malic acid may be present. The pulp also contains an acid or acids of the pectic type, possibly present as acid potassium salts and insoluble in alcohol.   T. S. P.

Application of the Biochemical Method to the Detection of Sucrose and Glucosides in Certain Ericaceæ. ÉMILE BOURQUELOT and (Mlle.) A. FICHTENHOLZ (*J. Pharm. Chim.*, 1913, [vii], 8, 158—164).—The presence of sucrose, of a β-glucoside which is hydrolysed by emulsin, and of invertase and emulsin is demonstrated in *Arbutus unedo, Arbutus Menziezii, Azalea mollis, Calluna vulgaris, Kalmia latifolia*, and *Vacinium myrtillus*.   E. F. A.

Plant Chemistry. P. Q. KEEGAN (*Chem. News*, 1913, 108, 61—62. Compare A., 1912, ii, 1085).—A brief résumé and discussion of our present knowledge of the occurrence and composition of the bitter principles, fat-oils, and oxydases in plants, special reference being made to analyses of the bearberry (*Arbutus uva-ursi*).   W. G.

The Nature of the Sugar Found in the Tuber of Arrowhead. K. MITAKE (*J. Biol. Chem.*, 1913, 15, 221—229).—Dextrose, lævulose, and sucrose were found; galactose and raffinose are doubtful; maltose, pentose, and mannose are absent.   W. D. H.

Capoc Seeds and Capoc Oil. HERMANN MATTHES and HEINRICH HOLTZ (*Arch. Pharm.*, 1913, 251, 376—396).—Capoc seeds, obtained from *Eriodendron anfractuosum* and other trees and plants allied to the *gossypium*, contain 7·5% of water, 25·6% of fatty oil, and 5·6% of ash; the last consists essentially of potassium phosphate, and contains also considerable quantities of calcium, magnesium, and sulphuric acid. Capoc oil, which is expressed from the seeds, is a pale yellow, viscous liquid, having a faint, pleasant odour and taste; after long keeping it deposits solid constituents. It resembles cotton-seed oil, with which it is often adulterated. The oil has D^{15} 0·9218, n^{40} 1·4630, and is optically inactive. It has iodine number 88·7 (93·3) [the numbers in brackets are the values given by a capoc oil extracted from the seeds by petroleum], acid number 21·6 (3·4—4·6), saponification number 192·3 (196·3), Reichert-Meissl value 0·8, and Polenske value 0·14—0·34. The m. p. of the fatty acids (Hehner's method) is 34—35° and the solidifying point 28—30°, the values of the m. p. and of the solidifying point being 36° and 31—32° respectively after the acids have been freed from phytosterol. The very high m. p. of the fatty acids serves to identify capoc oil in the presence of other oils, as also do Halphen's reaction Milliau's modification of Becchi's reaction, and the nitric

acid test. The behaviour of the oil with Welman's, Serger's, and Kreis's reagents, and in the elaidic acid test is also described. Capoc oil is a drying oil, but does not become hard even after four months' exposure.

Capoc oil consists essentially of the triglycerides of palmitic, oleic, and linolic acids. The fatty acids are 26—28% palmitic acid and 72—74% liquid acids (40% linolic acid and 60% oleic acid); volatile acids are present only in small quantity. The oil contains 1·04% of unsaponifiable matter.

The crude phytosterol obtained from the oil contains 74% of reddish-brown, slightly dextrorotatory liquid constituents (iodine number 74·7), and 26% of a solid *phytosterol*, m. p. 136°, $[\alpha]_D - 29·97°$ in alcohol and ether (*acetate*, m. p. 126°, needles).

C. S.

Presence of Quinine in the Seed of Cinchona Ledgeriana (Moens). P. VAN LEERSUM (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 153—155).—In order to investigate the formation of quinine in *Cinchona* the author has examined the seeds of *C. Ledgeriana*. The finely powdered seed was first extracted with light petroleum, which removed a pale green oil, D^{18} 0·930, $[\alpha]_D^{20} - 26°$, which formed 18·6% of the material, and then digested with lime and sodium hydroxide and extracted with benzene. The total alkaloid so obtained (about 0·38% of the dry seed) was purified, and finally concentrated as the hydrochloride on a microscope slide, when quinine was detected by the herapathite reaction (compare A., 1905, ii, 620).   J. C. W.

The Availability of Glucosamine Hydrochloride as a Source of Nitrogen for the Nutrition of Maize (Zea Mays) and Beans (Phaseolus multiflorus). MARSTON LOVELL HAMLIN (*J. Amer. Chem. Soc.*, 1913, **35**, 1046—1049).—When, for the purpose of comparison, the above-named plants were grown in an ordinary culture solution, in a nitrogen-free solution and in a solution containing glucosamine hydrochloride as the sole source of nitrogen, it was invariably found that the glucosamine had a deleterious effect, and caused withering.

It is evident, therefore, that under the conditions of the experiment, glucosamine cannot be utilised as a source of nitrogen for nutrition.   D. F. T.

A New Species of Prostanthera and its Essential Oil. R. T. BAKER and HENRY G. SMITH (*J. Roy. Soc., New South Wales*, 1913, **46**, 103—110).—The stalks and leaves of the new shrub, for which the name *Prostanthera cineolifera* is proposed, yield 0·71% of a yellow oil, which rapidly darkens on exposure to light. The crude oil has D^{15} 0·9204, n^{22} 1·4711, and is soluble in 1·7 volumes of 70% alcohol. After removal of phenols and aldehydes, the cleared oil has D^{15} 0·9199; n^{22} 1·4706, $\alpha_D + 4·1°$. Saponification number of ester + free acid = 9·9 by boiling and 8·5 by cold saponification with two hours' contact; saponification number after acetylation 34·2 by

boiling, 18·3 by cold saponification. It is probable that the principal ester in the oil of this plant is geranyl acetate, constituting 2·9% of the crude oil. The isolation of geraniol was not, however, practicable owing to the small quantity of oil obtainable. The phenols present constitute 0·65% of the oil, and are composed of carvacrol and thymol. Cuminaldehyde is present to the extent of 0·142%.

The main constituents of the oil are cineole (61 per cent.) and cymene. A small quantity of a dextrorotatory terpene, probably pinene, is also present, whilst, by the action of alcoholic potassium hydroxide on the portion of the oil boiling above 224°, a substance is obtained which is possibly a sesquiterpene, but the amount of which is insufficient for identification.   H. W.

Condition of Soil Phosphoric Acid Insoluble in Hydrochloric Acid. WILLIAM H. FRY (*J. Ind. Eng. Chem.*, 1913, 5, 664—665).— Whilst it is probable that soils may contain small quantities of phosphoric acid compounds which are not soluble in hydrochloric acid, mineralogical analyses have shown that a very large number of soils contain apatite (a soluble phosphate) enclosed in quartz grains. The quartz acts as a protective coating, and the phosphate is apparently insoluble in hydrochloric acid.   W. P. S.

Organic Soil Constituents in their Relation to Soil Fertility. OSWALD SCHREINER (*Eighth Inter. Cong. App. Chem.*, 1912, 15, 231—245).—In water-culture experiments with wheat, it was shown that creatinine, creatine, hypoxanthine, arginine, histidine, and nucleic acid are all assimilated, both when supplied as the only source of nitrogen and in presence of nitrate. When nitrates are present in addition to the organic compounds, there is a decrease in the amount of nitrate assimilated as compared with the amount when nitrate alone is supplied. The lowest decrease in nitrate absorbed was 17% with creatine, and the highest, 45%, with hypoxanthine. Further experiments on the effect of histidine, creatinine, and asparagine, used singly and together, showed increased growth with the single substances, in the order as given; and a further increase when all were present simultaneously, although the amount of nitrogen supplied was the same.   N. H. J. M.

Organic Phosphorus in the Soil. JOHN STEWART (*Eighth Inter. Cong. App. Chem.*, 1912, 15, 273—300).—The Grandeau method for estimating organic phosphorus in soils gives somewhat low results, since some of the phosphorus dissolves in the acid, and some remains undissolved after treatment with alkali. The method is, however, one of the best hitherto proposed.

The iron and aluminium of humus are organically combined, except the small amount in colloidal form.

The decaying organic matter of soils interacts with the phosphates present with production of various organic compounds containing phosphoric acid and the different bases. Acid and basic mineral phosphates are probably found as intermediate products.

Barium chloride, magnesia mixture (both in alkaline solutions), phenylhydrazine in faintly acid solution, and ammonium hydroxide in presence of sufficient iron or aluminium, reprecipitate inorganic phosphorus quantitatively in presence of organic matter, in some cases at least. No precipitate is formed in absence of organic matter.   N. H. J. M.

Biochemical Factors in Soils. MICHAEL X. SULLIVAN (*Eighth Inter. Cong. Appl. Chem.*, 1912, 15, 305—312).—The oxidising power of soils, as indicated by aloin, is greater in productive than in less productive soils, and in surface soils as compared with subsoils. The catalytic power of soils shows similar differences.

It is evident from the presence of such compounds as histidine, arginine, and cytosine, that soils contain enzymes, either intra- or extra-cellular. No soil extract has hitherto been found to contain diastatic, inverting, lipolytic, proteolytic, oxidising, or catalysing enzymes; and it has been found that when diastase is added to soil it is either fixed or destroyed in a few days.

The oxidising and catalysing powers of soils are probably due to the inorganic and organic substances rather than to enzymes. Both properties are retained for years by air-dried soils. Many substances present in soils result from the metabolism of micro-organisms. In mould cultures, fatty acids, especially oleic and palmitic acids, purine bases, such as guanine, adenine, and hypo-xanthine, histidine, and probably thymine, are present.
                                                              N. H. J. M.

Increasing the Manurial Action of Cyanamide under the Influence of Ferric Oxide. ALBERT STUTZER (*Eighth Inter. Cong. App. Chem.*, 1912, 15, 301—304).—The results of pot experiments with oats grown in sandy loam showed that the manurial value of cyanamide is increased by addition of molasses, owing to the increased production of carbon dioxide in the soil.

In further experiments, it was found that addition of ferric oxide, in the form of bog ore, greatly increased the yield of oats. It was found that ferric oxide accelerates the production of carbamide from cyanamide, and there may be a stimulating action in addition.

As a rule, 50 kilos. of bog ore per hectare will suffice.
                                                              N. H. J. M.

Boron as Catalytic Manure. HENRI AGULHON (*Eighth Inter. Cong. App. Chem.*, 1912, 15, 9).—In pot experiments with peas, haricots, beet, and radish, the yields were increased by boric acid up to 34%. In field experiments with oats, the yield was increased by 54% when 1·5 kilo. of boric acid per hectare was applied. Applications of 20—50 kilos. were found to be too much for wheat, oats, maize, lucerne, peas, colza, and lupines; the yields, weighed fresh, were frequently increased without any gain in dry matter.
                                                              N. H. J. M.

Organic Chemistry.

Preparation of Hydrocarbons with Two Conjugated Double Linkings. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 261642).—When $\alpha\gamma$-glycols of the general formula

$$\text{RRC(OH)·CHR·CR(OH)·CHRR}$$
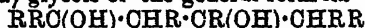
(where R is an alkyl group or hydrogen) are heated with agents that withdraw water, they furnish compounds of the general formula

$$\text{RRC:CR·CR:CRR.}$$

Butane-$\alpha\gamma$-diol when heated with 30% sulphuric acid at 170—180° yields a 10% yield of erythrene; with phosphoric acid at 300° the yield is 60%, and with magnesium sulphate at 300—400° about 50%, whilst β-methylbutane-$\beta\delta$-diol with potassium hydrogen sulphate at 160—170° gives rise to a 20% yield of isoprene.

$\alpha\alpha$-Dimethylerythrene, b. p. 74°, is obtained in 40% yield from β-methylpentane-$\beta\delta$-diol at 160° with aluminium chloride.

<div align="right">F. M. G. M.</div>

Diisobutenyl from Tribromoisobutane. VL. KRESTINSKI and K. KRIVOROTKO (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 946—949).—The action of magnesium on $\alpha\beta\gamma$-tribromoisobutane, $\text{CH}_2\text{Br·CMeBr·CH}_2\text{Br}$ (compare Pogorshelski, A., 1905, i, 315), in presence of ether and treatment of the product obtained with water, yields, as principal product, $\beta\epsilon$-dimethyl-$\Delta^{\alpha\epsilon}$-hexadiene, $\text{CH}_2\text{:CMe·CH}_2\text{·CH}_2\text{·CMe:CH}_2$, D^{20} 0·7512, n_D^{20} 1·4309 (compare Pogorshelski, A., 1899, i, 785). Treatment of the latter with hydrogen bromide yields the $\beta\epsilon$-dibromo-$\beta\epsilon$-dimethylhexane, $\text{CMe}_2\text{Br·CH}_2\text{·CH}_2\text{·CMe}_2\text{Br}$, m. p. 68°.

<div align="right">T. H. P.</div>

Preparation of Halogen Derivatives of the Paraffin Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 261677, 263716).—A satisfactory yield of chlorinated or brominated hydrocarbons is obtained by mixing the parent hydrocarbons in a gaseous condition with the vapour of the required halogen. Mixtures of chloro- and dichloro-, and of bromo- and dibromo-hexane were thus obtained; chloroisopentane furnished $\alpha\beta$-dichloro-β-methylbutane, whilst chloropentane gave rise to a *dichloropentane*, b. p. 130—150°. In the second patent it is shown that the halogenation can be effected by means of the silent electric discharge; thus n-pentane furnishes a mixture of α- and γ-chloropentane.

<div align="right">F. M. G. M.</div>

Addition of Bromine to Chlorinated Olefines. WALTHER HERZ and W. RATHMANN (*Ber.*, 1913, 46, 2588—2590. Compare this vol., ii, 26, 765).—The reactions between bromine and di-, tri-, and tetra-chloroethylene have been studied. Known quantities of the two substances, with or without diluents, were sealed up in test-tubes of dark brown glass, and kept at 25° for different intervals, when the tubes were broken under potassium iodide and the unabsorbed bromine

titrated. By employing a large excess of hydrocarbon the reaction could be expressed in the form, $1/t \log a/(a-x)$, where a is the initial concentration of bromine and x the amount absorbed after the time t.

cis-Dichloroethylene was found to absorb bromine nearly twice as fast as the *trans*-modification. No constant values could be obtained in the case of trichloroethylene, but *aaβ-trichloro-aβ-dibromoethane* was isolated as a pale yellow, pungent smelling liquid, b. p. 126°/85 mm. The influence of diluents was studied in the case of tetrachloroethylene.

<div align="right">J. C. W.</div>

The Action of Sodium Ethoxide on Tetranitromethane. A Caution. ALEXANDER K. MACBETH (*Ber.*, 1913, **46**, 2537—2538; *Chem. World*, 1913, **2**, 328).—The addition of sodium ethoxide to tetranitromethane may give rise to serious explosions.

In an experiment in which 30 grams of tetranitromethane were being treated with an alcoholic solution of sodium ethoxide, the formation and separation of the sodium derivative of trinitro-methane appeared to be proceeding in a normal manner when a violent explosion occurred doing serious damage to the experimenter and to the laboratory.

<div align="right">D. F. T.</div>

Mechanism of the Reactions between Alcohols and Mineral Acids. Oxonium Compounds of Hydrogen Haloids. ALEXEI E. FAVORSKI (*J. pr. Chem.*, 1913, [ii], **88**, 480—495. Compare McIntosh, T., 1904, **85**, 919; 1905, **87**, 784; A., 1905, i, 254, 677; 1906, i, 481, and Mokievski, A., 1899, i, 729).—Di*iso*propylcarbinol, ethyl*tert.*-butylcarbinol, and *iso*propyl*tert.*-butylcarbinol (this vol., i, 12) readily form with hydrogen haloids, crystalline oxonium salts of the following types:

$$(\text{I.}) \quad {\substack{R\\H}}{>}O{<}{\substack{H\\X}} \qquad (\text{II.}) \quad {\substack{R\\H}}{>}O{\diagup}^{\!H\ H}\!\!\!\!\diagdown O{<}{\substack{R.\\X}}$$
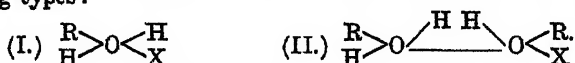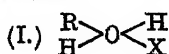
The compounds of the second type are the more stable, and are obtained by the action of the hydrogen haloid on the alcohols at 0° or the ordinary temperature; at lower temperatures compounds of the first type are produced. The oxonium compounds derived from glycols (Mokievski, *loc. cit.*) and diethylene ether are formulated as follows:

$$\begin{array}{c} CH_2 \cdot O {<}{\substack{H\\H}} \\ | \\ CH_2 \cdot O {<}{\substack{H\\X}} \end{array} \quad \text{and} \quad \begin{array}{c} CH_2 \cdot OH \cdot CH_2 \\ | \qquad | \qquad | \\ CH_2 \cdot OX \cdot CH_2 \end{array}.$$
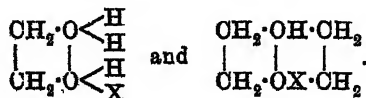
The author considers that the intermediate formation of oxonium compounds of this kind must be taken into account in explaining the mechanism of all reactions in which alcohol and mineral acids simultaneously take part, and illustrates his views by reference to the formation of ethers and hydrocarbons by the action of acids on alcohols, and the transformation of glycols into ketones and aldehydes under the influence of acids.

[With ANNA I. UMNOVA.]—The *compounds* of di*iso*propylcarbinol with hydrogen iodide and hydrogen bromide, $2C_7H_{15} \cdot OH, HX$,

separate in colourless crystals, m. p. 77—78° and 68—69° respectively, by passing the hydrogen haloids into the carbinol at the ordinary temperature; the corresponding *hydrochloride* is very hydroscopic.

[With P. Aschmarin.]—The following *compounds* of ethyl *tert.*-butylcarbinol are described: $2C_7H_{15}\cdot OH,HI$, m. p. 74—76°; $2C_7H_{15}\cdot OH,HBr$, m. p. 52—54°; $C_7H_{15}\cdot OH,HBr$, m. p. 13—17°; $C_7H_{15}\cdot OH,HCl$, m. p. 23—25°; $2C_7H_{15}\cdot OH,HCl$.

[With Ernst Fritzmann.]—The compounds of *iso*propyl*tert.*-butylcarbinol with hydrogen iodide, $2C_8H_{17}\cdot OH,HI$, and hydrogen bromide, $2C_8H_{17}OH,HBr$, have m. p. 78—80° and 77—78° respectively.

F. B.

The Spacial Arrangement of the Hydroxyl Groups of Polyhydroxy-compounds. The Configuration of the Saturated Glycols and of α- and β-Dextrose. Jacob Böeseken (*Ber.*, 1913, 46, 2612—2627).—The influence of hydroxy-compounds on the conductivity of boric acid solutions is set forth in a series of experiments, most of which have already been described (this vol., ii, 147; i, 742). The main conclusion arrived at by the author, that exaltation of the conductivity is caused by those compounds in which two hydroxyl groups attached to neighbouring carbon atoms are also in the same plane, thus permitting the formation of ring combinations with the boric acid, is further exemplified and extended to the determination of the configuration of saturated glycols and of α- and β-dextrose. Saturated glycols have no positive influence, and therefore the hydroxyl groups are arranged on opposite sides of the neighbouring carbon atoms. Alcohols with more than two hydroxyl groups are likely to have some pair or other in the favourable position, and glycerol, erythritol, β-nitro-αγδ-trihydroxy*iso*butane, pentaerythritol, mannitol, dulcitol, and sorbitol have positive influences in increasing degrees.

α- and β-Methylglucosides, sucrose, and raffinose have no pair of hydroxyl groups in the favourable position, and have only a minimal, negative influence on boric acid. α-Dextrose has a greater influence than β-dextrose, and the sugars are therefore represented by the formulæ I. and II. respectively, α-dextrose possessing one pair of neighbouring hydroxyl groups on the same side of the plane of the ring.

$$
\begin{array}{ll}
& H_2C\cdot OH \\
& OH\cdot CH \\
& \quad CH \\
(I.) \quad O\diagdown & HC\cdot OH \\
& OH\cdot CH \\
& OH\cdot CH
\end{array}
\qquad
\begin{array}{ll}
& H_2C\cdot OH \\
& OH\cdot CH \\
& \quad CH \\
(II.) \quad O\diagdown & HC\cdot OH \\
& OH\cdot CH \\
& HC\cdot OH
\end{array}
$$
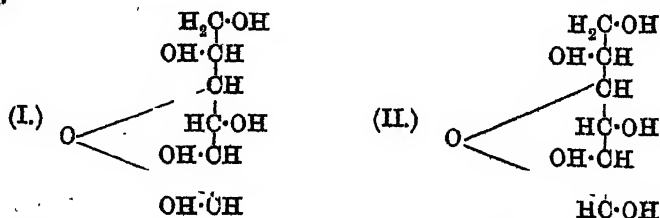
The gradual fall in the conductivity of α-dextrose–boric acid and the rise in conductivity of β-dextrose–boric acid coincide with the mutarotation, and the constants for the mutarotation and the alteration in

conductivity are equal. If the mutarotation were accompanied by the opening of the ring, a chain of five labile hydroxyl groups would be formed, and the conductivity of the boric acid solution would be increased. The fact that this does not happen supports E. F. Armstrong's view that mutarotation takes place without disturbing the γ-oxide ring (T., 1903, **83**, 1305).   J. C. W.

Conversion of Cellulose into Dextrose. HERMANN OST (*Ber.*, 1913, **46**, 2995—2998).—In reply to the interpretation placed by Willstätter and Zechmeister (this vol., i, 955) on the optical activity of the dextrose obtained by Ost and Wilkening (A., 1910, i, 364) from the hydrolysis of starch by sulphuric acid, the author maintains that the other experiments of the latter investigators supply final evidence that the yield of dextrose was in reality over 90% of the starch used, and attributes the low optical activity to the well known considerable effect of the presence of traces of impurity.   D. F. T.

Electrical Conductivity of Some Platinum Compounds of Organic Disulphides. LEO A. TSCHUGAEV and A. KOBLJANSKI (*Zeitsch. anorg. Chem.*, 1913, **83**, 8—26).—In order to avoid the complications introduced by water, the author has examined the conductivity of a large number of complex compounds in methyl alcohol. It is found that compounds of the type $[PtS''Cl_2]$, where S'' is a dithioether, are non-conducting, but that further addition of disulphide causes a rapid increase of conductivity. An equilibrium occurs: $[PtS''Cl_2] + S'' \rightleftharpoons [Pt2S'']Cl_2$, the latter compound then becoming ionised.

The compounds of ethylene-dithioglycol ethers have been compared with those from propylene-dithioglycol ethers. The platinum chloride compound of the *diethyl ether*, $[PtCl_2,C_3H_6(SEt)_2]$, crystallises in needles, m. p. 135°, and the *di-n-propyl ether* compound has m. p. 133°. It has not been found possible to prepare sufficiently pure compounds from aa- and $a\epsilon$-dithioglycol ethers, but the conductivity of mixed solutions of these sulphides with stable $a\beta$-compounds has been determined. The aa-dithio-ethers have the least tendency to form complexes.

The conclusions are in accordance with Werner's co-ordination theory.   C. H. D.

Compounds of Platinous Nitrite with Organic Dithio-ethers. LEO A. TSCHUGAEV and WITALIUS G. CHLOPIN (*Zeitsch. anorg. Chem.*, 1913, **82**, 401—419. Compare A., 1910, i, 354; 1912, i, 70).—Like the halogen compounds, platinous nitrite readily forms isomeric compounds with dithio-ethers. The bimolecular compound is the first product, and is more stable than in the case of the halogen compounds, so that the conversion into the unimolecular form takes place much less readily. The latter modifications are most readily obtained from the chlorides and soluble nitrites.

Diethyl ethylene dithioether and platinous nitrite form a *compound*, $[Pt2C_2H_4(SEt)_2]Pt(NO_2)_4$, m. p. 170—170·5°. It reacts with Reiset's chloride to form the yellow compound $[Pt4NH_3]Pt(NO_2)_4$. The former

compound is also obtained from the bimolecular chloride and sodium nitrite. The unimolecular *compound*, $C_2H_4(SEt)_2,Pt(NO_2)_2$, has m. p. 161—161·5°, and does not react with Reiset's chloride. Excess of the ether, together with potassium platinonitrite, convert it into the bimolecular modification.

Dimethyl ethylene dithioether and platinous nitrite yield the bimolecular *compound,* $[Pt2C_2H_4(SMe)_2]Pt(NO_2)_4$, m. p. 214·5—215°, which is slowly converted, even in the cold, into the unimolecular compound, m. p. 210·5—211°, by an excess of the ether.

The dipropyl dithioether also yields two *compounds*, m. p. 184·5—185° and 179—179·5° respectively, and the *compounds* from the di-n-butyl dithioether have m. p. 181—181·5° and 172—172·5° respectively.

Diethyl propylene dithioether yields a *compound* with m. p. 229—229·5°, the constitution of which is uncertain.

Diethyl β-hydroxypropylene $\alpha\gamma$-dithioether yields a sparingly soluble *compound*, m. p. 182—182·5° (decomp.), and probably bimolecular.

Dimethyl sulphide yields only a unimolecular compound with platinous nitrite, all attempts to prepare a bimolecular modification having failed. C. H. D.

Complex Compounds of Organic Sulphides with Quadrivalent Platinum. LEO A. TSCHUGAEV and J. BENEVOLENSKI (*Zeitsch. anorg. Chem.*, 1913, **82**, 420—425).—Isomerism has not hitherto been observed in compounds of quadrivalent platinum with organic sulphides. It is now found that compounds with two complex ions are obtained from hydrogen platinichloride and sulphides, but that their composition does not correspond with the expected formulæ.

Methyl sulphide and platinic chloride yield a precipitate with the empirical composition $Pt,2Me_2SCl_3$, which at 110—115° suddenly changes from red to yellow, yielding a mixture of two substances, which may be separated by means of chloroform. The less soluble compound, $PtCl_4,2Me_2S$, darkens from 150°, whilst the other,

$$PtCl_2,2Me_2S,$$
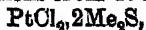
has m. p. 157°. The original compound is thus $[Pt,4Me_2S]PtCl_6$. A similar compound is obtained from diethyl ethylene dithioether.
C. H. D.

Formic Acid as a Solvent. OSSIAN ASCHAN (*Chem. Zeit.*, 1913, **37**, 1117—1118).—The solubilities of a number of inorganic salts and organic compounds in 95% formic acid are given. A wide range of metallic salts is found to dissolve in this acid, but not so freely as in water. Easily reduced salts are liable to decomposition, but, whereas iodine is liberated from sodium iodide in the cold, potassium iodide is stable. The acid decomposes pinene nitrosochloride and the salts of weak organic acids, and esterifies certain alcohols, such as borneol. With these exceptions, it is a useful solvent for many organic compounds, including in addition to bromo-carboxylic acids, for which it has already received frequent application, polycyclic hydrocarbons, terephthalic acid, uric acid, indigotin, and alizarin.

The acid is easily volatilised on the water-bath, and deposits large

crystals of many substances, as, for example, suberic acid, citric acid, α-bromocamphor, α-nitronaphthalene, and m-dinitrobenzene. It is now cheaper than glacial acetic acid, and usually exhibits a greater difference of solvent power between the hot and cold liquid, and, in spite of its blistering effect, it is deserving of more extensive application.   J. C. W.

Displacement of Acetic Acid from Solutions of its Salts by Carbon Dioxide Under High Pressure. VLADIMIR N. IPATIEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 992—994. Compare Ipatiev and Verchovski, A., 1909, ii, 564; 1911, ii, 716).—The author has investigated the action of carbon dioxide under a pressure of 50 atmospheres on aqueous solutions of various acetates, both at the ordinary temperature and at 90°. With 12% calcium acetate solution, crystalline calcium carbonate was precipitated in some cases, but not in others; in one instance, 1 gram of the carbonate was obtained from 50 c.c. of the acetate solution after seven days at 90°. In a similar manner barium acetate yields the carbonate, and copper acetate the basic carbonate, $CuCO_3,Cu(OH)_2,H_2O$, but no precipitate was obtained from nickel acetate, even after several months.   T. H. P.

The Action of Acetic Anhydride on Ferric and Chromic Nitrates. RUDOLF F. WEINLAND and HANS REIHLEN (*Zeitsch. anorg. Chem.*, 1913, **82**, 426—430).—The compounds described by Späth (A., 1912, i, 408) as normal ferric and chromic acetates are really acetates of the triferri-(chromi)hexa-acetato-base, and the method of preparation has no advantage over those usually adopted. Both compounds yield the characteristic platinichlorides.   C. H. D.

Production of Hydrocarbons from a Solution of Sodium Stearate by Electrolysis. H. T. F. RHODES (*Chem. News*, 1913, **108**, 201).—The production of hydrocarbons by the electrolysis of aqueous solutions of the salts of aliphatic acids increases in difficulty with increasing molecular weight of the acid, probably owing to the partial hydrolysis which occurs when the salts are dissolved in water. By employing a small current, however, the author has succeeded in electrolysing an aqueous solution of sodium stearate which had been acidified with acetic acid, and has obtained a hydrocarbon very similar in physical properties to paraffin wax. The substance could only be detected after the solutions had been preserved for some time, and could not be identified owing to the small yield.   H. W.

Oxidising Action of Potassium Permanganate in an Alkaline Medium on Normal, Saturated Fatty Acids. EVGENJI S. PRSHEVALSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 891—905; *J. pr. Chem.*, 1913, [ii], **88**, 495—501. Compare A., 1911, i, 947).—The action of faintly alkaline potassiumpermanganate solution on various acids of the aliphatic series has been investigated.

With 1% permanganate solution, n-heptoic acid gives (1) valeric, butyric, and propionic acids; (2) a ketonic acid, probably
$$CH_3 \cdot [CH_2]_4 \cdot CO \cdot CO_2H,$$

m. p. 51—52°; (3) a dibasic dihydroxy-acid, $C_5H_8(OH)_2(CO_2H)_2$, and (4) adipic, glutaric, succinic, and oxalic acids. Under similar conditions, *n*-hexoic acid yields glutaric acid, in addition to the acids already mentioned (*loc. cit.*). *n*-Valeric acid gives butyric, propionic, oxalic, and succinic acids. At either 37—38° or 100°, *n*-butyric acid yields oxalic and propionic acids, whilst if 5% permanganate is used, β hydroxybutyric and *iso*malic acids are also formed. Propionic acid gives carbon dioxide and oxalic acid, and if the oxidation is carried out in a solution containing 5% of alkaline hydroxide, hydroxypropionic acid.

The results obtained show that the difficulty of oxidising normal fatty acids increases with the shortness of the carbon-atom chain (compare Margulies, A., 1894, i, 491), and that the products obtained vary with the conditions of oxidation. In every case oxidation takes place at two points of the carbon-atom chain: (1) at the carbon atom adjacent to the carboxyl group, the next lower fatty acid being formed, and (2) at the carbon atom next to the methyl group.

Since the dibasic acids obtained never contained the same numbers of carbon atoms as the original acids, but always one less, the methyl group must undergo oxidation to carboxyl and then to carbon dioxide.

That oxidation of two carbon atoms simultaneously in one molecule of an acid may take place is shown by the formation of a dihydroxy-dicarboxylic acid from *n*-heptoic acid. As intermediate products of these oxidations, hydroxy- and keto-acids are formed.

In view of the ready oxidisability of the methyl group, which is adjacent to a partly oxidised carbon atom, the possibility of the formation of acetic acid in these oxidations seems doubtful.

With *n*-butyric acid, oxidation is accompanied by isomerisation of the normal propyl group to the iso-group.   T. H. P.

Lignoceric Acid. HANS MEYER, LEO BROD, and WALTHER SOYKA (*Monatsh.*, 1913, **34**, 1113—1142).—Lignoceric acid is shown to occur in the "solid paraffin" fraction of tar distilled from Bohemian lignite. With a view to ascertaining whether lignoceric acid, $C_{24}H_{48}O_2$, has the normal structure it has been degraded to $C_{22}H_{44}O_2$ (A., 1904, i, 548; 1905, i, 405, 736), and attempts have also been made to synthesise it from normal behenic acid, $C_{22}H_{44}O_2$. The degradation product is not identical with behenic acid, and the synthetic product is not lignoceric acid, so that the latter cannot be the normal 24 carbon saturated fatty acid.

Lignoceric acid, $C_{24}H_{48}O_2$, m. p. 80—80·5°, prepared from ground-nut oil, on treatment with bromine in presence of amorphous phosphorus yields *a-bromolignoceric acid*, m. p. 68·5°, which crystallises in colourless rhombohedra and on treatment with sodium ethoxide in dry alcohol furnishes with some difficulty *a-ethoxylignoceric acid*, m. p. 61—62°, crystallising in slender, colourless needles. *Methyl a-bromo-lignocerate*, m. p. 46—47°, forms small, colourless crystals. The bromo-acid when boiled with potassium iodide in alcohol yields *a-iodolignoceric acid*, m. p. 74°, which forms small, colourless prisms from a mixture of light petroleum and acetic acid, and when treated with potassium

hydroxide furnishes a mixture of *a-hydroxylignoceric acid* (m. p. 92°, small crystals) with the *unsaturated acid*, $C_{24}H_{46}O_2$, m. p. 59°, which forms a crystalline mass. The latter acid on oxidation with permanganate yields oxalic acid and *isobehenic acid*, $C_{22}H_{44}O_2$, m. p. 75°. The latter crystallises in glancing pearly leaflets, and furnishes a *methyl* ester, m. p. 54°, as colourless leaflets, and a crystalline *lithium* salt, m. p. 210° (decomp.). Melting-point curves for mixtures (1) of behenic and *iso*behenic acids, and (2) of the methyl esters of the two acids are given.

Behenic acid, m. p. 82—84°, was prepared by the catalytic reduction of erucic acid, and converted successively into the chloride (leaflets, m. p. 73—75°); methyl ester, m. p. 55°; amide, m. p. 111°, and the latter reduced to docosyl alcohol by means of sodium in amyl alcohol and this was converted into docosyl iodide, m. p. 46°. The latter was condensed with ethyl malonate to *docosylmalonic acid*, and this heated until carbon dioxide was no longer evolved when it yielded a *tetracosanic acid*, $C_{24}H_{48}O_2$, m. p. 85·5—86°, crystallising in pearly leaflets, and furnishing a *methyl* ester (m. p. 59·5—60°, glancing scales), a crystalline *lithium* salt, and an *a-bromo*-derivative, m. p. 73·5°, the *methyl* ester of which has m. p. 57°, and crystallises in glancing leaflets. Melting-point curves and tables for mixtures (1) of synthetic tetracosanic acid and lignoceric acid, and (2) of the methyl esters of these two acids are given.

In the synthesis of the tetracosanic acid the principal product is a *ketone*, $C_{47}H_{94}O$, which was not further characterised.

The synthetic method described was also used in preparing arachidic acid, m. p. 77°, from octadecyl iodide (compare Baczewski, A., 1897, i, 11). Melting-point curves for mixtures of lignoceric acid with (*a*) arachidic acid, (*b*) stearic acid, and (*c*) palmitic acid are given.

T. A. H.

Montanic Acid. HANS MEYER and LEO BROD (*Monatsh.*, 1913, **34**, 1143—1157. Compare Easterfield and Taylor, T., 1911, **99**, 2302).—Montanic acid has been exhaustively examined and purified by methods described in detail in the original, and shown to have the formula, $C_{28}H_{56}O_2$, first suggested by Ryan and Dillon (A., 1909, i, 629). A number of its derivatives are described.

Montanic acid melts at 85° and crystallises from acetic acid in small, pearly leaflets. The *chloride*, m. p. 67·5—68·5°, forms masses of leafy crystals and is readily soluble in benzene or petroleum. The *amide*, m. p. 112°, separates from alcohol as a crystalline powder. *a-Bromomontanic acid*, m. p. 77°, forms colourless scales from a mixture of acetic acid and light petroleum; with sodium ethoxide in alcohol, it yields *a-ethoxymontanic acid*, m. p. 71—72°, crystallising from acetic acid in colourless scales, and with ethyl alcohol in presence of mineral acids, *ethyl bromomontanate*, m. p. 62—63°, which forms colourless leaflets from alcohol. Attempts to eliminate hydrogen bromide and form the corresponding unsaturated acid were successful. T. A. H.

Ground-nut (Earth-nut) Oil. HANS MEYER and ROBERT BEER (*Monatsh*, 1913, **34**, 1195—1208).—The numerous researches already

conducted on the composition of ground-nut oil render it probable that it contains glycerides of arachidic, lignoceric, oleic and linoleic acids, and leave doubtful the presence of glycerides of palmitic, stearic, and hypogaeic acids. The authors confirm the occurrence in the oil of glycerides of the four first-named acids and also of palmitic acid, but they were unable to find any evidence of stearic or hypogaeic acid in the fatty acids prepared from the oil (compare Franz, *Diss.*, München, 1910). The supposed stearic acid obtained by Hehner and Mitchell's method (A., 1897, ii, 289) lowers the melting point of stearic acid and in reality consists of a mixture of arachidic and lignoceric acids. No trace of dihydroxypalmitic acid could be found in the oxidation products from the unsaturated fatty acids of ground-nut oil so that hypogaeic acid cannot be a constituent of these acids. Tables and curves of the melting points of mixtures of arachidic acid with (*a*) stearic acid and (*b*) palmitic acid are given in the original.

<div align="right">T. A. H.</div>

Candelilla Wax. HANS MEYER and WALTHER SOYKA (*Monatsh.*, 1913, **34**, 1159—1172. Compare Olsson-Seffer, *Bull. Imp. Inst.*, 1909, **7**, 411; Hare and Bjerregard, *J. Ind. Eng. Chem.*, 1910, **2**, 203; Deiler, *ibid.*, p. 454; Sanders, P., 1911, **27**, 250, and *Anal. Inst. Nac. Med. Mex.*, 1905, **7**, 498, and Niederstadt, *Chem. Zeit*, 1911, **35**, 1190).—Candelilla wax on extraction with hot alcohol yields 18 to 20% of soluble soft resin, which gives the Liebermann-Storch reaction. The portion of the resin-free wax soluble in hot alcohol, but insoluble in the cold, consists principally of dotriacontane, not hentriacontane as Sanders (*loc. cit.*) supposed, which was isolated by extraction with ether and amounted to 74 to 76% of the crude wax. The remaining constituent not removed by ether is a lactone, $C_{30}H_{58}O_3$, m. p. 88°, which forms a colourless, crystalline mass, is neutral in reaction, but yields a *potassium* salt when boiled with potassium hydroxide in alcohol, and is partly esterified when treated with methyl alcohol and sulphuric acid. This substance appears to be that which Sanders mistook for myricyl alcohol (*loc. cit.*), and which Fraps and Ruther (*J. Ind. Eng. Chem.*, 1910, **2**, 454) described as a hydrocarbon. It is perhaps identical with Darmstädter and Lifschütz's lanoceric acid lactone (A., 1896, i, 522).

The authors doubt whether the hydrocarbon frequently found in plants and described as hentriacontane really consists of the latter.

<div align="right">T. A. H.</div>

Water of Crystallisation of the Calcium Salt of Lauronolic Acid. CHARLES E. BURKE (*J. Amer. Chem. Soc.*, 1913, **35**, 1647—1648).—Although the rapid evaporation of a solution of calcium lauronolate on a water-bath gives surface crystals containing approximately $3H_2O$ (Noyes and Burke, A., 1912, i, 159), yet under the conditions of Bredt's method with slower evaporation (A., 1911, i, 417) the crystals, which separate in this case under the liquid, contain exactly $2H_2O$, as stated by Bredt.

<div align="right">D. F. T.</div>

Preparation of Di-iodotariric Acid. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 261211. Compare A., 1892, 470).—*Di-iodo-*

tariric acid, colourless needles, m. p. 48·5°, containing 47·5% of iodine and of therapeutic value, is obtained when a boiling aqueous solution of tariric acid containing sodium hydroxide is slowly treated with 9 parts of a mixture of iodine (100 parts), potassium iodide (160 parts), and water (740 parts); the product is separated by the addition of dilute sulphuric acid.   F. M. G. M.

The Ability of Alcoholic Hydroxyl Groups to Form Complexes. II. GENNARO CALCAGNI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 157—162. Compare A., 1910, i, 811; Weinland and Herz, A., 1912, i, 854).—The *basic glycollate* of a *hexaglycollatotriferri*-base, $[Fe_3(OH)_2(CO_2 \cdot CH_2 \cdot OH)_6] \cdot CO_2 \cdot CH_2 \cdot OH(FeOH)_3$, prepared by fractional precipitation of an alcoholic solution with ether, is an orange-yellow, amorphous substance which is hygroscopic and readily hydrolyses. The *basic nitrate*, $[Fe_3(OH)_2(CO_2 \cdot CH_2 \cdot OH)_6]NO_3 \cdot Fe(OH)_3$, is similar in properties. The *basic lactate* of a *hexalactatotriferri*-base,

$$[Fe_3(OH)_2(CO_2 \cdot CHMe \cdot OH)_6]CO_2 \cdot CHMe \cdot OH \cdot Fe(OH)_3, 4H_2O,$$
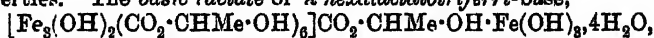
is an orange-yellow, hygroscopic substance which is readily hydrolysed. When solutions of chrome alum and sodium benzoate are mixed, *chromous benzoate*, $Cr(CO_2Ph)_2, H_2O$, is precipitated. *Ferrous salicylate*, $Fe(CO_2 \cdot C_6H_4 \cdot OH)_2$, is a reddish-violet, amorphous substance. *Chromous salicylate* was also prepared.   R. V. S.

Complex Oxalic Derivatives of Iridium. ALEXIS DUFFOUR (*Ann. Chim. Phys.*, 1913, [viii], 30, 169—240).—A detailed, connected account of work already published (Abstr., 1909, i, 762—763; 1910, i, 541; 1911, i, 519; 1912, ii, 849). Apart from slight modifications of some of the views expressed already, the following new results are now recorded. *Thallous iridotetrachloro-oxalate*, $Tl_3IrCl_4C_2O_4$, forms maroon-coloured, microscopic, hexagonal lamellæ, which are pleochroic and faintly birefringent. *Argentous iridotetrachloro-oxalate* resembles the thallous salt, but only assumes a crystalline texture after prolonged contact with water.   T. A. H.

Electrolytic Reduction of Aldehydes. WILHELM SCHEPSS (*Ber.*, 1913, 46, 2564—2574).—An extension of the earlier investigation (Tafel and Schepss, A., 1911, i, 784) in which it was demonstrated that by electrolytic reduction the aldehyde group in anisaldehyde can be directly converted into the methyl group. The reduction of the aldehydes was effected in a mixture of alcohol and sulphuric acid.

Propaldehyde undergoes reduction to propane less readily than does acetone, and it was found that cathodes of lead or cadmium are much more effective than a mercury cathode. No formation of any organic lead or mercury compounds analogous to those observed in the reduction of acetone could be detected.

Reduction of heptaldehyde yielded *n*-heptane, and again the action proceeds less easily than with methyl *iso*amyl ketone (Tafel, A., 1909, i, 766). Benzaldehyde (compare Kauffmann, A., 1899, i, 152; Law, T., 1907, 91, 755) at a cadmium cathode gave as hydrocarbon product a small quantity of toluene; no benzene could be detected (compare

Law, *loc. cit.*). *p*-Hydroxybenzaldehyde could be reduced to *p*-cresol ; salicylaldehyde and *m*-hydroxybenzaldehyde appeared to undergo reduction only as far as the corresponding alcohols, and in attempts to reduce the former more energetically much resinification occurred.

Protocatechualdehyde gave 3 : 4-dihydroxytoluene, whilst vanillin gave the corresponding ether, 4-hydroxy-3-methoxytoluene. The experiments in the latter case were conducted with cadmium electrodes and the result is somewhat at variance with that of Law (*loc. cit.*). Piperonal underwent reduction to hydropiperoin and *methylenedioxytoluene*, an aromatic oil, b. p. 81—83°/11 mm., 197—198° (corr.)/741·5 mm., D_{10}^{16} 1·1353, n_D^{16} 1·53165.

When reduced in solution in the usual mixture of alcohol, and sulphuric acid, *p*-dimethylaminobenzaldehyde was converted into the corresponding alcohol, which immediately condensed with the alcohol of the solvent ; the product was therefore p-*dimethylaminobenzyl ethyl ether*, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot OEt$, a liquid of characteristic amine odour, b. p. 269—271°/747 mm. ; *methiodide*, m. p. 141·5—143°. Reduction of the aldehyde in alcohol-free diluted sulphuric acid gave as chief product *p*-dimethylaminobenzyl alcohol, as a viscous oil, b. p. 175—178°/28 mm. (compare Rousset, A., 1895, i, 176).

In the above examples it was generally found that the process of reduction became more speedy and complete with increased temperature and current density. The extent to which reduction was effected varied considerably, however, in different cases.

A repetition of the reduction of citral (Law, T., 1912, 101, 1025, 1544) at a lead cathode certainly yielded a red product at the cathode, but it was of a resinous nature and not an organic lead compound.   D. F. T.

Formation of Methylglyoxal. CARL NEUBERG and W. OERTEL (*Biochem. Zeitsch.*, 1913, 55, 495—503).—The importance of methylglyoxal as an intermediary product of sugar degradation has been often discussed, and the substance has been obtained directly from dextrose by various methods (distillation in presence of weak alkalis, zinc carbonate, etc.). It is now shown that it can be obtained from sugars in larger quantities if solutions of these substances are heated with sodium carbonate or disodium hydrogen phosphate in the presence of phenylhydrazine. Particularly good yields were obtained in this way from lævulose, and moderate yields from dextrose. Mannose also yielded a small quantity. The methylglyoxal was in each case identified in the form of an osazone.   S. B. S.

Plant Colloids. III. Processes of Solution and Removal of the Ash of Starch. MAXIMILIAN SAMEC and F. VON HOEFFT (*Koll. Chem. Beihefte*, 1913, 5, 141—210. Compare A., 1912, ii, 144).—The influence of the removal of the ash from starch on the physicochemical properties of starch solutions has been studied, and the properties of solutions of such starch are compared with those of ordinary starch solutions prepared under identical conditions. It is shown that the three processes, removal of the ash, solution and ageing

occasion the same changes in the properties of starch solutions, namely, decrease of the viscosity, and decrease of the influence of acids and bases on the viscosity. These changes take place more rapidly the higher the temperature. At constant temperature in solutions of different concentrations the viscosity decreases in the same proportion in the same time. Simultaneously with the decrease of viscosity an increase in the electrical conductivity is brought about, and the electric transport and amount precipitated by alcohol decrease. The osmotic pressure is slightly decreased, whilst the optical rotation slightly increases and the quantity of titratable acid increases. Starch granules give practically no free electrolyte to water at ordinary temperatures, but at the swelling temperature this occurs fairly rapidly, and at the same time the power of the granules for taking up water increases in a series of sudden steps. The observations lead to the assumption that the ash of starch is present as an amylphosphoric acid, and this assumption brings observations of other observers into agreement.   J. F. S.

Chemistry of Starch. Schardinger's Crystalline Dextrins. II. Hans Pringsheim and Franz Eissler (*Ber.*, 1913, 46, 2959—2974. Compare A., 1912, i, 832).—Further observations on dextrin-β (hexa-amylose), dextrin-α (tetra-amylose), and their scission products are recorded and the properties of the crystalline "slime" prepared by Schardinger are described. Provisional formulæ for diamylose and *iso*-diamylose are advanced and discussed.

Schardinger's "slime" $[(C_6H_{10}O_5)_2]x, C_2H_5 \cdot OH$, was prepared by dissolving crude dextrin (precipitated by means of chloroform from the liquid produced by the action of *Bacillus macerans* on starch paste) in hot water, heating to remove chloroform and then diluting with water, when the slime was precipitated. It was isolated by means of a centrifuge, and crystallised from water containing 1·5% alcohol, when it formed hexagonal tablets. It has $[\alpha]_D^{20} + 139 \cdot 2°$. On acetylation in presence of zinc chloride, it yields the hexa-acetate of diamylose (*loc. cit.*) and by the Baumann-Schotten method yields the *dibenzoate* of *diamylose*, m. p. 200° (approx.), an amorphous substance also obtained when tetra-amylose is benzoylated by this process, an observation which indicates that the slime belongs to the α-group of dextrins. Triamylose, the scission product of dextrin-β, yields a *tribenzoate*, m. p. 190°, which is also amorphous.

These amyloses (dextrins) all yield additive products with iodine when their aqueous solutions are treated with iodine in potassium iodide. The iodine additive products of the α-group form green-tinted needles, become blue when moistened with water, but form dark red solutions when much water is added ; those of the β-group form dark reddish-brown prisms, and give dark red solutions with water. *Tetra-amylose iodide*, $(C_6H_{10}O_5)_4, 1\frac{1}{2}I$, and *hexa-amylose di-iodide*, $(C_6H_{10}O_5)_6 \cdot 2I$, belonging respectively to these groups, have been prepared ; the slime gives an iodide of the α-type.

When tetra-amylose is dissolved in glycerol by heating, and the liquid is heated at 200° during thirty minutes, a small part of the dextrin is converted into the slime and a little into *isodiamylose*, a new

amorphous amylose of the β-type. The latter is also obtained in the form of its amorphous *hexa-acetate* when tetra-amylose is acetylated with acetic anhydride in presence of sulphuric acid. Similarly, hexa-amylose when heated in water for a long time yields a small amount of the slime, and when acetylated in presence of sulphuric acid yields iso*triamylose-nonoacetate*, from which on hydrolysis iso*triamylose* is obtained; both these products are also amorphous. These new amyloses are hygroscopic, dextrorotatory, decompose without melting when heated, and reduce Fehling's solution. Some preliminary observations on the acetylation of "soluble" starch are also recorded.

Starch was separated by Gatin-Gružewska's method (A., 1911, i, 357) into amylopectin and Maquenne's amylose. These two products on treatment with *Bacillus macerans* fermented less easily than starch, but yielded the same products, viz., tetra-amylose, hexa-amylose, and the slime.

Takadiastase and *Penicillium africanum* hydrolyse hexa-, tetra-, tri-, and di-amyloses, whilst emulsin decomposes *iso*tri- and *iso*di-amyloses, but has no action on the other four. Yeast and diastase do not act on any of the six dextrins.   T. A. H.

Hexabromoplatinates [Platinibromides]. ALEXANDER GUTBIER and A. RAUSCH (*J. pr. Chem.*, 1913, [ii], 88, 409—424. Compare A., 1910, i, 12; 1911, i, 32).—On account of their sparing solubility and superior powers of crystallisation, the platinibromides may be employed with advantage for the characterisation of amines in place of the platinichlorides.

A solution of hydrogen platinibromide, suitable for this purpose, is readily obtained by dissolving platinic chloride in 20—30 times its weight of hydrobromic acid (D 1·49), and evaporating its solution to half its bulk.

The platinibromides have no definite m. p., but become dark and sinter before liquefaction takes place.

The compounds described below form light red to dark red crystals having a magnificent lustre:

Tetramethylammonium platinibromide, $(NMe_4)_2PtBr_6$, lustrous, red crystals of octahedral habit. *Tetraethylammonium platinibromide*, felted crystals.

Tripropylammonium platinibromide, compact clusters of deep red, rhombic, double pyramids.

Diisobutylammonium platinibromide, elongated prisms. *Triisobutylammonium platinibromide*, small, red crystals. iso*Amylammonium platinibromide*, bright red crystals. *Diisoamylammonium platinibromide*, tabular crystals. *Triisoamylammonium platinibromide*, bright red prisms. *Allylammonium platinibromide*. *Guanidine platinibromide*, $C_2H_{12}N_6PtBr_6$, lustrous, red crystals of a complicated structure. *Triphenylguanidine platinibromide*,

$$2NPh\text{:}C(NHPh)_2,H_2PtBr_6,$$
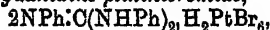
slender, felted, orange-red needles.

Nitrosodimethylammonium platinibromide, $(NO\cdot NHMe_2)_2PtBr_6$, acicular, pleochroic prisms. *Nitrosodiethylammonium platinibromide*, dark red, fibrous crystals. *Nitrosodipropylammonium platinibromide*,

red prisms. *Nitrosodiisobutylammonium platinibromide,* dark red, felted crystals.

m-*Chlorophenylammonium platinibromide,* $(C_6H_4Cl\cdot NH_3)_2PtBr_6$, lustrous, red plates. p-*Chlorophenylammonium platinibromide,* bright red, elongated prisms. 2 : 4-*Dichlorophenylammonium platinibromide,* dark red platelets.

o-*Bromophenylammonium platinibromide,* prisms combined, with pyramids. m-*Bromophenylammonium platinibromide,* small, dark red, felted crystals. p-*Bromophenylammonium platinibromide,* red, fibrous crystals.

m-*Nitrophenylammonium platinibromide,* prisms. p-*Nitrophenyl-ammonium platinibromide,* elongated prisms. p-*Nitrosophenyldi-methylammonium platinibromide,* $(NO\cdot C_6H_4\cdot NHMe_2)_2PtBr_6$, deep red, felted crystals.

o-*Tolyldimethylammonium platinibromide,* $(C_6H_4Me\cdot NHMe_2)_2PtBr_6$, lustrous, red plates.

p-*Tolyldimethylammonium platinibromide,* red plates. 2 : 4-*Tolylene-diammonium platinibromide,* $C_7H_{12}N_2PtBr_6$, deep red prisms. 3 : 4-*Tolylenediammonium platinibromide,* vivid red prisms.

o-*Methoxyphenylammonium platinibromide,* vivid red, monoclinic prisms. p-*Methoxyphenylammonium platinibromide,* long, slender, lustrous, red prisms. o-*Ethoxyphenylammonium platinibromide,* stellar, feebly pleochroic discs, or long prisms. p-*Ethoxyphenylammonium platinibromide,* lustrous, red, fibrous crystals.

Tribenzylammonium platinibromide, dark red crystals. *Benzyl-methylammonium platinibromide,* dark red prisms.

Benzylidenemethylammonium platinibromide,
$$(CHPh\vcentcolon NHMe)_2PtBr_6,$$
red, felted aggregates. *Benzylidene-ethylammonium platinibromide,* leaflets.

Phenylbenzylammonium platinibromide, dark red crystals. *Phenyl-benzylmethylammonium platinibromide,* $(NHMePh\cdot C_7H_7)_2PtBr_6$, red, felted crystals. *Phenylbenzylideneammonium platinibromide,* elongated prisms. 2 : 4 : 5-*Trimethylphenylammonium platinibromide,* light red prisms.

3-*Methylpyridinium platinibromide,* dark red, regular crystals. *Dimethylpyridinium platinibromide,* dark red, felted crystals. *Tri-methylpyridinium platinibromide,* clusters of deep red crystals. *Piperidinium platinibromide,* elongated prisms. iso*Quinolinium platinibromide,* lustrous, red, prismatic crystals.   F. B.

Action of Ammonia on β-Aminocrotonates and β-Carb-ethoxyaminocrotonates. ERNST PHILIPPI (*Monatsh,* 1913, **34**, 1187—1193. Compare this vol., i, 598).—It is argued that the substance which Meister (A., 1888, 675) regarded as having the formula $OEt\cdot C(OH)(NH_2)\cdot CH\vcentcolon CMe\cdot NH\cdot CO\cdot NH_2$, may be equally well represented by the formula
$$CH_3\cdot CH(NH\cdot CO\cdot NH_2)\cdot CH(NH_2)\cdot CO_2Et$$
or $CH_3\cdot C(NH_2)(NH\cdot CO\cdot NH_2)\cdot CH_2\cdot CO_2Et$, so far as the reactions described by Meister are concerned. The author finds that the substance on treatment with hot alkali solution yields ethyl β-amino-.
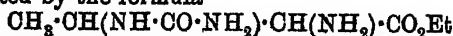
crotonate, and that the latter condenses with carbamide in dry alcohol to regenerate the parent substance, which must therefore be ethyl β-amino-β-carbamidobutyrate represented by the third formula given above.

It is remarkable that whilst the substance is formed by the action of alcoholic ammonia at 160—170° on ethyl β-aminocrotonate, it is not produced when liquefied ammonia is allowed to react with the ester in the cold even for several days. It is probable that in the former case part of the ester is decomposed with the formation of carbamide, which then condenses with the rest of the ester. **T. A. H.**

The Condensation of Carbamides with Esters. GEORG ROEDER (*Ber.*, 1913, **46**, 2560—2564).—In an attempt to prepare hydurilic acid from ethyl ethanetetracarboxylate and carbamide, Conrad (A., 1907, i, 985) obtained scarcely a trace of the desired substance, although the analogous reaction with guanidine in place of carbamide proved satisfactory. It is now shown that the reaction with carbamide follows a different course from that expected, giving rise to *ethanetetra-carboxydi-imide*, which carbonises at 270ᶜ. The reaction was effected in warm alcoholic solution containing sodium ethoxide, and can be represented as : $CH(CO_2Et)_2 \cdot CH(CO_2Et)_2 + 2CO(NH_2)_2 =$

$$NH\mathopen{<}^{CO \cdot CH \cdot CO}_{CO \cdot CH \cdot CO}\mathclose{>}NH + 2NaOCN + 4EtOH.$$
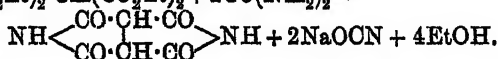
With thiocarbamide, the ester behaves as ethyl dimalonate, and under similar conditions to the last gives rise to *dithiohydurilic acid*, according to the equation : $CH(CO_2Et)_2 \cdot CH(CO_2Et)_2 + 2CS(NH_2)_2 =$

$$CS\mathopen{<}^{NH \cdot CO}_{NH \cdot CO}\mathclose{>}CH \cdot CH\mathopen{<}^{CO \cdot NH}_{CO \cdot NH}\mathclose{>}CS + 4EtOH ;$$ the product, which is unaltered at 250°, gives a yellow *pyridine* salt, and when suspended in water is coloured green by ferric chloride ; it can be desulphurised to hydurilic acid by heating at 100° with concentrated sulphuric acid.

As might be expected from the above results, ethyl succinate condenses with carbamide under similar conditions to the above with formation of succinimide and sodium cyanate. It is suggested that in this and the analogous case above, the course of the reaction follows the stages : $CH_2(CO_2Et) \cdot CH_2 \cdot CO_2Et \longrightarrow \mathopen{}^{CH_2 \cdot CO}_{CH_2 \cdot CO}\mathclose{>}N \cdot CO \cdot NH_2 \longrightarrow$

$\mathopen{}^{CH_2 \cdot CO}_{CH_2 \cdot CO}\mathclose{>}NH + NH_2 \cdot CO_2Et$; the last substance, the formation of which is attributed to the action of the alcohol on the primary condensation product, then decomposes under the influence of sodium ethoxide into alcohol and sodium cyanate.

When ethyl phthalate is subjected to this reaction, either with carbamide or thiocarbamide, the product is phthalimide. **D. F. T.**

Chloro-glyoxime, Oxime Derivatives of Oxalyl Chloride and Oxalyl Semichloride, and Cyanoformylchloride Oxime. JOSEF HOUBEN and H. KAUFFMANN (*Ber.*, 1913, **46**, 2821—2835).—By careful chlorination in cold hydrochloric acid solution, both chloro-

amphi- and chloro-*anti*-glyoxime are converted into the same dichloro-*anti*-glyoxime. The chloro-*anti*-glyoxime is the more readily chlorinated. It is established that fuming hydrogen chloride converts chloro-*amphi*-glyoxime into the *anti*-modification contrary to the statement of Hantzsch, (A., 1892, 693).

Dichloro*anti*glyoxime, $OH \cdot N{:}CCl \cdot CCl{:}N \cdot OH$, has decomp. 221° when crystallised from water, or 212° when crystallised from toluene. It gives a reddish-brown coloration with ferric chloride.

Dichloroglyoxime diacetate, $OAc \cdot N{:}CCl \cdot CCl{:}N \cdot OAc$, separates in well formed crystals, m. p. 162—163°. Dry ammonia gas converts it into dioximino-ethylenediamine, which differs from the known compound, firstly, in forming a *diacetyl* derivative, m. p. 206° when crystallised from water, or 212° when crystallised from chloroform, and secondly, in not yielding a dibenzoyl derivative. The difference is attributed to a changed configuration.

Thionyl chloride converts chloro*amphi*glyoxime into *chloro-oximino-acetonitrile*, $OH \cdot N{:}CCl \cdot CN$. This is purified by distillation and the crystals formed, which are extremely hygroscopic, filtered and dried in a current of air in a specially constructed apparatus. It has m. p. 55—56°; the vapour has a very irritant action. It crystallises in monoclinic prisms and plates giving no coloration with ferric chloride until it has been warmed with water for a few seconds. The substance is a mixture of the two forms :

$$\begin{array}{ccc} Cl \cdot C \cdot CN & & Cl \cdot C \cdot CN \\ \| & \text{and} & \| \\ HO \cdot N & & N \cdot OH \end{array}$$

, in which one greatly preponderates. The form present in the smaller proportion is much more easily decomposed by water. Probably the conversion of one form into the other takes place during the distillation.

Solution of the nitrile in water yields very soon a voluminous, flocculent precipitate which does not contain halogen. Its investigation is not yet completed, but it is probably *dioximino-oxalonitrile* $NC \cdot C(N \cdot OH) \cdot C(N \cdot OH) \cdot CN$. It explodes violently at 250—260°.

Whereas both chloro-*amphi*- and *anti*-glyoxime diacetate and chloro-*amphi*-glyoxime monoacetate distil unchanged in a vacuum, the *anti*-diacetate at the ordinary pressure is decomposed, losing acetic acid and forming *chloro-oximinoacetonitrile acetate*, $CN \cdot CCl{:}N \cdot OAc$, a clear liquid, b. p. 74—75°/13 mm.

Fuming hydrochloric acid converts it into *chloro-oximinoacetamide*, $OH \cdot N{:}CCl \cdot CO \cdot NH_2$, which crystallises in well-formed, pointed needles, m. p. 162°, crystallised from water, or 166° crystallised from benzene (decomp.).

On acetylation, *acetoximinochloroacetamide*, $OAc \cdot N{:}CCl \cdot CO \cdot NH_2$, m. p. 134°, is formed. This compound serves to distinguish the oximinoacetamide from the chloroglyoximes.

The *hydrochloride* of *chloro-oximinoacetiminomethyl ether*,

$$OH \cdot N{:}CCl \cdot CCl(NH_2) \cdot OMe,$$
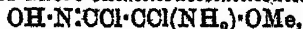
forms crystals, m. p. 161°. The analogous *ethyl* ether has m. p. 155—164° according to the rate of heating.

When hydrolysed in fuming hydrochloric acid, *chloro-oximinoacetic acid*, $OH \cdot N{:}CCl \cdot CO_2H$, is formed. This has m. p. 125° (decomp.)

The acid is also obtained from chloro-oximinoacetic ester as prepared by Jovitschitsch (A., 1906, i, 732).

It has a strong acid astringent and yet sweet taste. It gives a deep, dark red coloration with ferric chloride. E. F. A.

Crystals of Diamminedimethylglyoximinecobalt Chloride. D. N. Arteméev (*Zeitsch. Kryst. Min.*, 1913, **52**, 632; from *Ann. Inst. Mines, St. Petersburg*, 1910, 2). Crystals of Chloroammine-dimethylglyoximinecobalt. D. N. Arteméev and D. Th. Muraschev (*ibid.*, 1913, **52**, 627—628; from *ibid.*, 1910, 2, 272—274). Crystals of Nitroaquodimethylglyoximinecobalt. D. N. Arteméev and W. M. Lomberg (*ibid.*, 1913, **52**, 632—633; from *ibid.*, 1910, **2**, 352—356).—Descriptions are given, in Fedorov's nomenclature, of the crystals of these compounds prepared by L. A. Tschugaev (A., 1906, i, 814). Their formulæ are respectively $Co(NH_3)_2D_2H_2Cl,5H_2O$, $CoNH_3ClD_2H_2$, and $CoNO_2D_2H_2,H_2O$, where

$$D = \begin{matrix} CH_3 \cdot C:NO \\ | \\ CH_3 \cdot C:NO \end{matrix}$$

L. J. S.

Complex Compounds of Rhodium. Leo A. Tschugaev and W. Lebedinski (*Zeitsch. anorg. Chem.*, 1913, **83**, 1—7).—Rhodium forms complex compounds with a-dioximes, completely resembling those of tervalent cobalt (A., 1906, i, 814; 1907, i, 904). Two series of compounds are formed, one being salts of a mono-acid base, $[Rh,2NH_3,D_2H_2]X$, and the other salts of a monobasic complex acid, $[RhCl_2D_2H_2]H$ (D = dimethylglyoxime, X = halogen). The complex acid is remarkably stable.

Diamminedimethylglyoximinerhodium chloride,

$$[Rh,2NH_3,D_2H_2]Cl,5H_2O,$$
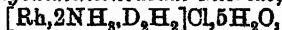
from dimethylglyoxime and chloropentamminerhodium chloride at 150°, crystallises from hot water. The *iodide* is anhydrous. The *nitrate* is precipitated in microscopic tablets; the *perchlorate*, *platini-chloride*, and *platinibromide* are very insoluble.

Rhodidichlorodimethylglyoximinic acid, $[RhCl_2,D_2H_2]H$, from sodium rhodihexachloride and dimethylglyoxime, boiled with water, crystallises from water containing a little hydrochloric acid. The *ammonium* salt, with $1H_2O$, forms large, brownish-yellow crystals. The *guanidinium* salt is anhydrous and sparingly soluble. C. H. D.

Decomposition of Alkylidenehydrazines. Nicolai M. Kishner (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 973—986).—The action of magnesium methyl iodide on *cyclo*butanecarboxylamide yields acetyl-*cyclo*butane, b. p. 137—139°/761 mm., and the latter, on decomposition of its hydrazone, gives *ethylcyclobutane*, $CH_2 \overset{CH_2}{\underset{CH_2}{<}} > CHEt$, b. p. 70°/754 mm., D_0^0 0·7461, D_0^{20} 0·7284, n_D^{15} 1·4032, n_D^{20} 1·4004, which is extremely stable towards permanganate, towards fuming hydrobromic acid in a sealed tube at 100°, and unlike derivatives of three-membered rings, towards concentrated sulphuric acid at the ordinary temperature. Reduction of ethyl*cyclo*butane by means of fuming hydriodic

acid in a sealed tube at 210° yields γ-methylpentane, but no *n*-hexane ; as would be expected from the presence of a CH-group in the molecule, γ-methylpentane is readily attacked by fuming nitric acid.

1 : 1-Dimethyl*cyclo*pentane (compare A., 1908, i, 864) may be obtained by distilling 1 : 1-dimethyl-2-*cyclo*pentanonehydrazone (A., 1911, i, 42) with potassium hydroxide and platinised porous tile.
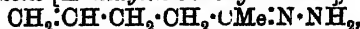
Allylacetonehydrazone [Δ^a-*hexylen*-ε-*onehydrazone*],
$$CH_2:CH \cdot CH_2 \cdot CH_2 \cdot CMe:N \cdot NH_2,$$
b. p. 187—188°/757 mm., $D_0^{17\cdot5}$ 0·8990, mixes with water in all proportions and, when distilled with potassium hydroxide and platinised porous tile, yields Δ^a-*hexene*, $CH_2:CH \cdot CH_2Pr$, b. p. 64°/756 mm., D_0^{20} 0·6734, n_D^{20} 1·3870.

Distillation of β-methyl-Δ^β-hepten-ζ-onehydrazone with potassium hydroxide and platinised porous tile yields β-*methyl*-Δ^β-*heptene*, $CMe_2:CH \cdot CH_2Pr$, b. p. 122·4°/756 mm., D_0^{20} 0·7254, n_D^{20} 1·4169, which gives β-methylheptane (compare Clarke, A., 1911, i, 345) on reduction by Sabatier and Senderens' method, and forms the *nitrosochloride*, $CMe_2Cl \cdot C(:NOH) \cdot CH_2Pr$, m. p. 48—51°, this exhibiting normal cryoscopic behaviour in benzene. By removal of hydrogen chloride from the nitrosochloride, conversion of the oxime thus obtained into the corresponding ketone, and distillation of the hydrazone of this ketone with potassium hydroxide and platinised porous tile, β-methyl-Δ^β-heptene is again obtained.

Distillation of pentan-α-ol-δ-onehydrazone gives *n*-amyl alcohol.

βζ-Dimethyl-Δ^β-octene, $CMe_2:CH \cdot CH_2 \cdot CH_2 \cdot CHMeEt$, obtained by distillation of the hydrazone of the keto-alcohol,
$$OH \cdot CMe_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHMeEt$$
(A., 1911, i, 1027), with potassium hydroxide and platinised porous tile, seems to be identical with the hydrocarbon obtained from citronellaldehydehydrazone (A., 1911, i, 1027). T. H. P.
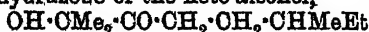
Complex Mercury Compounds from Ethylene and Carbon Monoxide. WALTER SCHOELLER, WALTER SCHRAUTH, and WALTER ESSERS (*Ber.*, 1913, 46, 2864—2876).—Mercury acetate in methyl alcohol reacts with a molecule of ethylene to form *acetatomercuriethyl methyl ether*, $CH_2 \cdot CO \cdot O \cdot Hg \cdot CH_2 \cdot CH_2 \cdot OMe$, crystallising in colourless, slender, pointed needles, m. p. 42°. The *bromide* of the ether forms bunches of needles, m. p. 58°; the *iodide* crystallises in stellate aggregates of needles or platelets.

In presence of ethyl alcohol reaction between the mercury salt and ethylene is slower, and *acetatomercuridiethyl ether*,
$$CH_2 \cdot CO \cdot O \cdot Hg \cdot C_2H_4 \cdot OEt,$$
is formed. This sinters at 33°, m. p. 36°. The *chloride* crystallises in colourless needles, m. p. 92°.
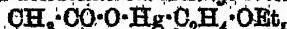
When carbon monoxide is substituted for ethylene, *methyl acetatomercuriformate*, $CH_2 \cdot CO \cdot O \cdot Hg \cdot CO \cdot OMe$, is formed. It crystallises in stellate aggregates of needles, m. p. 110° (corr. decomp.). The *chloride* separates in long needles, m. p. 110° (corr. decomp.); the *bromide* is composed of colourless platelets, decomp. 127—128°, and the *iodide* is similar in appearance.

Treatment with hydrogen sulphide in methyl alcohol gives rise to

the formation of *methyl sulphidomercuriformate*, $S(Hg \cdot CO \cdot OMe)_2$, obtained as a colourless, cheese-like precipitate.

Mercury acetate ethyl formate crystallises in aggregates of needles which sinter at 65°, decomp. 125°. The *chloride* forms plates, m. p. 88° (corr. decomp.); the *bromide* and *iodide* are very similar. The *sulphide* was obtained as a yellowish-white precipitate.　　E. F. A.

Decomposition of Pyrazoline Bases. Conversion of Phorone into 1:1-Dimethyl-2-*iso*butenyl*cyclo*propane. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 957—972).—The similarity in structure between mesityl oxide and phorone suggests the possibity of transforming the latter ketone into a pyrazoline base and thence into a hydrocarbon containing a trimethylene ring (compare A., 1912, i, 245). This possibility has been realised by the author.

Phorone and hydrazine react according to the equation:

$$CMe_2 \colon CH \cdot CO \cdot CH \cdot CMe_2 + N_2H_4 \longrightarrow CMe_2 \colon CH \cdot C \underset{N—NH}{\overset{CH_2 \cdot CMe_2}{<}}.$$
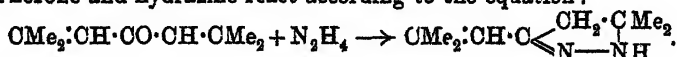
When distilled with potassium hydroxide in presence of platinised porous tile, this pyrazoline base decomposes in two ways, giving (1) 1:1-dimethyl-2-*iso*butenyl*cyclo*propane, or (2) the trimethylpyrazoline and acetone, $CMe \underset{N—NH}{\overset{CH_2 \cdot CMe_2}{<}} + COMe_2.$

1:1-*Dimethyl-2-isobutenylcyclopropane*, $CH_2 \underset{CH \cdot CH \colon CHMe_2}{\overset{CMe_2}{<}}$, is a liquid, b. p. 132°/758 mm., D_0^{20} 0·7677—0·7681, n_D 1·4414—1·4420. Although the chemical properties of this hydrocarbon are in complete accord with the structure given above, yet the magnitude of the molecular refraction is virtually identical with that calculated for a compound with two double linkings; this exaltation may depend on the relation of the trimethylene ring to the grouping $\colon CMe_2$, such relation possibly resembling that between two conjugated double linkings.

Oxidation of 1:1-dimethyl-2-*iso*butenyl*cyclo*propane by means of 1% potassium permanganate solution proceeds according to the scheme:

$$CH_2 \underset{CH \cdot CH \colon CMe_2}{\overset{CMe_2}{<}} \longrightarrow CH_2 \underset{CH \cdot CH(OH) \cdot CMe_2 \cdot OH}{\overset{CMe_2}{<}} \longrightarrow$$

$$CH_2 \underset{CH \cdot CO \cdot CMe_2 \cdot OH}{\overset{CMe_2}{<}} \longrightarrow CH_2 \underset{CH \cdot CO_2H}{\overset{CMe_2}{<}} + CH_3 \cdot COMe \ ;$$
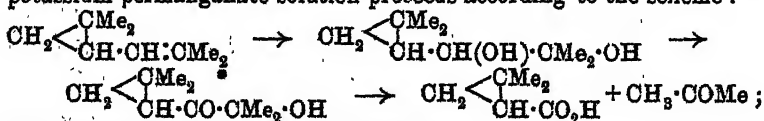
the intermediate glycol was not isolated.

The *ketol*, $CH_2 \underset{CH \cdot CO \cdot CMe_2 \cdot OH}{\overset{CMe_2}{<}}$, is a viscous liquid with an odour resembling terpineol, b. p. 200°/758 mm., D_0^{16} 0·9377, D_0^{20} 0·9347, $n_D^{16 \cdot 5}$ 1·4500, n_D^{20} 1·4490; it exhibits an optical exaltation of 1·43, although that due to the trimethylene ring is usually less than 1. Its *semicarbazone*, $C_9H_{16}O \colon N_2H \cdot CO \cdot NH_2$, m. p. 127°, and its *phenylurethane*, $C_9H_{15}O \cdot O \cdot CO \cdot NHPh$, crystallise in needles.

1:1-*Dimethylcyclopropane-2-carboxylic acid*, $CH_2 \underset{CH \cdot CO_2H}{\overset{CMe_2}{<}}$, is an oily liquid, b. p. 198°/751 mm., D_0^{18} 0·8990, n_D 1·4385, optical exaltation 0·83; it is stable towards alkaline permanganate solution.

Reduction of 1 : 1-dimethyl-2-*iso*butenyl*cyclo*propane by the method of Sabatier and Senderens, either at 120—125° or at 170°, yields a mixture of (1) a *cyclo*propane derivative, probably 1:1-dimethyl-2-*iso*butyl*cyclo*propane, and (2) $\beta\beta\epsilon$-*trimethylhexane*,

$$CMe_3 \cdot CH_2 \cdot CH_2 \cdot CHMe_2,$$
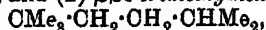
b. p. 124—125°/763 mm., D_0^0 0·7082—0·7086, n_D 1·3987—1·3998. Treatment of the 1 : 1-dimethyl-2-*iso*butyl*cyclo*propane with hydrogen bromide and subsequently with 2% potassium hydroxide solution yields $\beta\gamma\epsilon$-*trimethylhexan-β-ol*, OH·CMe$_2$·CHMe·CH$_2$·CHMe$_2$, b. p. 171—172°/755 mm., D_0^{20} 0·8316, n_D 1·4313.

1 : 1-Dimethyl-2-*iso*butenyl*cyclo*propane combines rapidly with 1 mol. of hydrogen bromide, giving the *monobromo*-derivative,

$$CH_2 {<}^{CMe_2}_{CH \cdot CH_2 \cdot CMe_2Br} \text{ or } CH_2 {<}^{CMe_2}_{CH \cdot CHBr \cdot CHMe_2},$$
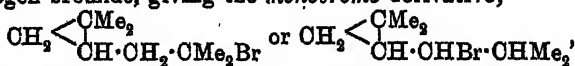
b. p. 94—96°/31 mm., D_0^{20} 1·1046, whilst the prolonged action of hydrogen bromide yields $\delta\zeta$-*dibromo-$\beta\zeta$-dimethylheptane*,

$$CHMe_2 \cdot CH_2 \cdot CHBr \cdot CH_2 \cdot CMe_2Br,$$
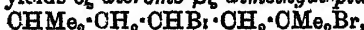
b. p. 134—136°/31 mm., D_0^{20} 1 3846. When distilled with aniline, both the mono- and dibromo-compounds yield $\beta\zeta$-*dimethyl-$\Delta^{\beta\delta}$-heptadiene*, CMe$_2$:CH·CH:CH·CHMe$_2$, which contains a small admixture of another hydrocarbon with different positions of the double linkings and has the following approximate physical constants: b. p. 139—141°/758 mm., D_0^{20} 0·7482—0·7510, n_D 1·4456—1·4470. Reduction of this hydrocarbon by Sabatier and Senderens' method at 170° results in the formation of $\beta\zeta$-dimethylheptane. T. H. P.

Decomposition of Pyrazoline Bases. Conversion of Cinnamaldehyde into Phenyl*cyclo*propane. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 949—957).—*Phenylcyclopropane*, CHPh${<}^{CH_2}_{CH_2}$, prepared by distilling phenylpyrazoline (from cinnamaldehyde and hydrazine) in presence of potassium hydroxide and platinised porous tile, is a liquid, b. p. 173·6°/758 mm., D_0^{15} 0·9449, D_0^{20} 0·9401, n_D^{15} 1·5342. Under the influence of moderately dilute sulphuric acid, it is converted into the same dimeride, $C_{18}H_{20}$, of α-phenyl-Δ^α-propylene as is obtained by boiling the latter with sodium.

Phenyl*cyclo*propane combines slowly with hydrogen bromide, yielding *o-bromopropylbenzene*, CHPhBr·CH$_2$Me, b. p. 129—130°, 43 mm., D_0^{15} 1·3124, n_D 1·5528. When boiled with aqueous potassium hydroxide, the latter gives (1) the hydrocarbon, $C_{18}H_{20}$, referred to above; (2) phenylethylcarbinol, and (3) allylbenzene, which is also obtained when α-bromopropylbenzene is distilled in presence of quinoline.

In acetic acid solution, the action of bromine on phenyl*cyclo*propane results mainly in the replacement of the nuclear hydrogen, combination of bromine with the trimethylene ring occurring to a very limited extent:

$$CHPh{<}^{CH_2}_{CH_2} + Br_2 \longrightarrow C_6H_4Br \cdot CH{<}^{CH_2}_{CH_2} +$$

$$HBr \longrightarrow C_6H_4Br \cdot CHEtBr.$$
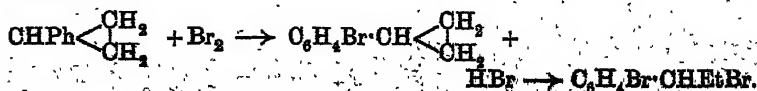
The last compound readily loses hydrogen bromide, giving the unsaturated bromo-derivative, $C_6H_4Br \cdot CH:CHMe$, which yields *p*-bromobenzoic acid on oxidation.

αγ·Dibromopropylbenzene, $CHPhBr \cdot CH_2 \cdot CH_2Br$ (?), formed in small proportion in the action of bromine on *cyclo*propane in acetic acid solution, crystallises in prisms, m. p. 125°.

4-Bromo-1-allylbenzene, $C_6H_4Br \cdot CH:CHMe$, is a liquid, b. p. 240—241°/764 mm., 124°/20 mm., D_0^{18} 1·3147, n_D 1·5692; owing to the conjugated nature of the double linkings in the ring and the side-chain, it exhibits optical exaltation. On reduction by means of hydriodic acid in a sealed tube, it yields propylbenzene. T. H. P.

Decomposition of Pyrazoline Bases : Synthesis of 1-Methyl-2-*iso*propyl*cyclo*propane. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 987—992).—iso*Butylideneacetone* [*β-Methyl-Δγ-hexylene-ε-one*], $CHMe_2 \cdot CH:CH \cdot COMe$, prepared by the condensation of *iso*butyraldehyde and acetone in presence of sodium hydroxide, is a liquid, b. p. 156°/757 mm., D_0^{18} 0·8484, n_D^{18} 1·4394 ; its *semicarbazone*, $C_7H_{13}N \cdot NH \cdot CO \cdot NH_2$, forms hexagonal plates, m. p. 162—163°.

3-*Methyl*-5-*iso*propyl*pyrazoline*, $NH \overset{\displaystyle CHPr^\beta \cdot CH_2}{\underset{\displaystyle N \!=\!=\! CMe}{<}}$, prepared by the action of hydrazine hydrate on *iso*butylideneacetone, is a liquid, b. p. 188·5—189·5°/754 mm., D_0^{17} 0·9081, n_D 1·4640 ; it oxidises readily in the air, its hot vapours igniting. Its *thioureide*, $C_7H_{13}N_2 \cdot CS \cdot NHPh$, crystallises in needles, m. p. 95—100°.

1-*Methyl*-2-*iso*propyl*cyclo*propane, $CH_2 \overset{\displaystyle CHMe}{\underset{\displaystyle CHPr^\beta}{<}}$, prepared by decomposition of the preceding compound in a sealed tube at 230°, is a liquid, b. p. 80—81°/748 mm., D_0^{20} 0·7102, n_D^{20} 1·3927, which is extremely stable towards potassium permanganate, combines slowly with bromine in acetic acid solution, and reacts vigorously with fuming nitric acid with formation of a heavy oil. Reduction of 1-methyl-2-*iso*propyl*cyclo*propane by Sabatier and Senderens' method takes place less readily than that of 1 : 1 : 2-trimethyl*cyclo*propane, but at 170° it seems to yield a mixture of *ββ*-dimethylpentane and *βγ*-dimethylpentane. With fuming hydrobromic acid it yields *γ-bromo-ββ-dimethylpentane*, b. p. 158—161°/763 mm., D_0^{20} 1·1585, n_D 1·4548, which gives *ββ*-dimethylpentane on reduction with hydriodic acid. T. H. P.

Catalytic Reactions at High Temperatures and Pressures. XXXII. VLADIMIR N. IPATIEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 994—995. Compare this vol., i, 693, 694).—In presence of nickel oxide, indene unites with hydrogen at 250—260° and 110 atmospheres, yielding *octahydrindene*, $\overset{\displaystyle CH_2 \cdot CH_2 \cdot CH \cdot CH_2}{\underset{\displaystyle CH_2 \cdot CH_2 \cdot CH \cdot CH_2}{}} > CH_2$, which is a liquid, b. p. 165—166°/767 mm., D^{20} 0·8334, n_D^{20} 1·46287 (compare Padoa and Fabris, A., 1908, i, 255). T. H. P.

Metaquinonoids. OTTO STARK, O. GARBEN, and L. KLEBAHN, (*Ber.*, 1913, **46**, 2542—2544. Compare this vol., i, 362, 849).—It is

found that the hydrocarbon, m-*xylylene*, described earlier decomposes at 303—305°, the lower figure given previously being due to insufficient drying.

The substance in the solid state is in a polymerised condition, but the chloroform solutions give ebullioscopic results agreeing with a depolymerised unimolecular product; the solution in chloroform is, however, much more sensitive than that in benzene. The benzene solutions of the substance obtained in the original preparation exhibit a decided fluorescence, and dye paper and linen, whilst the chloroform solutions of the previously separated substance do not possess these characteristics.

A preliminary examination of the absorption spectra of the two solutions indicated complete analogy with the behaviour of Thiele's tetraphenyl-*p*-xylylene; an absorption of blue and violet light which commenced in the green portion of the spectrum was observed both with the chloroform and the original benzene solutions.   D. F. T.

Elimination of Halogen Acids by Phosphoric Oxide. I. HANS LECHER (*Ber.*, 1913, **46**, 2664—2668).—Recent publications by Leuchs and his co-workers (this vol., i, 855, 972), in which mention is made of the catalytic action of compounds of phosphorus on the elimination of hydrogen chloride from certain acid chlorides, have led the author to publish a preliminary account of the use of phosphoric oxide in this direction.

Benzoyl chloride does not react with an excess of naphthalene at 180—200°. If, however, a small quantity of phosphoric oxide is added, a vigorous evolution of hydrogen chloride occurs, at the conclusion of which a mixture of much α- and less phenyl β-naphthyl ketone can be isolated, the total amount being 90% of that theoretically possible. Phosphoric oxide has the advantage over aluminium chloride that only small quantities of it are necessary, larger amounts having an unfavourable influence on the course of the reaction. On the other hand, the requisite temperature is high, and, in those cases in which the b. p. of the mixture lies below this temperature, the operation must be performed in sealed tubes. In these circumstances, the liberated hydrogen chloride can only be removed periodically, and greatly diminishes the velocity of the reaction. Thus, only small yields of benzophenone could be obtained by this method from benzoyl chloride and benzene.

Boiling benzyl chloride rapidly and completely eliminates hydrogen chloride in the presence of phosphoric oxide, forming a mixture of hydrocarbons which has not yet been completely investigated. ω-Chlorotriphenylmethane is similarly decomposed at about 150° into 9-phenylfluorene and much triphenylmethane.

A series of experiments has been performed to determine the exact nature of the catalyst. Bailey and Fowler (T., 1888, **53**, 755) have shown that phosphoric oxide reacts with hydrogen chloride according to the equation: $P_4O_{10} + 3HCl = POCl_3 + 3HPO_3$, but the author finds that no appreciable action occurs within a reasonable time at temperatures up to 260°, and, hence, that phosphoryl chloride cannot

be the actual catalyst. Direct experiment with metaphosphoric acid has shown that this substance is also inactive.

Finally, the active catalyst can easily be recovered by the removal of organic matter by extraction with benzene. In this manner, a mixture of a phosphorus compound (which yields metaphosphoric acid with water) and small quantities of carbon is obtained, which can be employed in the same manner as fresh phosphorus pentoxide.

H. W.

Morphological Studies in the Benzene Series. IV. The Crystalline Form of Sulphonates in Relation to their Molecular Structure. ERNEST H. RODD (*Proc. Roy. Soc.*, 1913, *A*, 89, 292—313. Compare T., 1910, 97, 1578; A., 1912, i, 756).— A number of salts of *p*-dichlorobenzenesulphonic acid have been prepared, and their crystallographic constants have been compared. Lanthanum *p*-dichlorosulphonate, $La(C_6H_3Cl_2SO_3)_3,15H_2O$, is deposited from solution between 10° and 50°; it forms triclinic prisms, which rapidly effloresce [$a:b:c = 1.6193:1:1.6028$; $a = 76°26'$; $\beta = 113°48'$; $\gamma = 68°6'$]. Neodymium *p*-dichlorobenzenesulphonate,
$$Nd(C_6H_3Cl_2SO_3)_3,12H_2O,$$
crystallises in short, thick, rose-coloured, monoclinic prisms between 15° and 50°, closely isomorphous with $Gd(C_6H_3Br_3SO_3)_3,12H_2O$ [$a:b:c = 0.5872:1:0.3810$; $\beta = 76°34'$]. Praseodymium *p*-dichlorobenzenesulphonate, $Pr(C_6H_3Cl_2SO_3)_3,12H_2O$, forms pale green, monoclinic prisms isomorphous with the corresponding neodymium salt [$a:b:c = 0.5887:1:0.3819$; $\beta = 76°26'$]. A salt of the composition $Pr(C_6H_3Cl_2SO_3)_3,15H_2O$, isomorphous with the corresponding lanthanum salt, is formed when a supersaturated solution is allowed to spontaneously crystallise at the ordinary temperature. A number of other sulphonates have also been prepared and measured. Gadolinium *p*-dibromobenzene sulphonate, $Gd(C_6H_3Br_2SO_3)_3,7H_2O$, monoclinic prisms [$a:b:c = 1.2595:1:0.6031$; $\beta = 89°16'$]. Didymium benzenesulphonate, $Di(C_6H_5\cdot SO_3)_3,9H_2O$, crystallises from a mixture of aqueous alcohol and ethyl acetate in thin, hexagonal-shaped plates belonging to the rhombic system [$a:b:c = 2.0795:1:1.9374$]. Potassium *p*-dichlorobenzenesulphonate, $C_6H_3Cl_2SO_3K$, crystallises anhydrous from aqueous solutions between 20° and 37° in thin, monoclinic prisms [$a:b:c = 1.5054:1:0.7636$; $\beta = 83°27'.5'$]. Sodium *p*-dichlorobenzenesulphonate, $C_6H_3Cl_2SO_3Na,H_2O$, crystallises in large, monoclinic tablets at 37° [$a:b:c = 3.0529:1:1.9583$; $\beta = 88°46'$]. Zinc *p*-dichlorobenzenesulphonate, $Zn(C_6H_3Cl_2SO_3)_2,8H_2O$, forms long, monoclinic prisms, which are always distorted [$a:b:c = 2.9985:1:2.4539$; $\beta = 79°20'$]. Magnesium *p*-dichlorobenzenesulphonate,
$$Mg(C_6H_3Cl_2SO_3)_2,8H_2O,$$
crystallises in stout, monoclinic, hemimorphic plates [$a:b:c = 2.9970:1:2.4450$; $\beta = 79°41'.5'$]. Ferric *p*-dibromobenzenesulphonate, $Fe(C_6H_3Br_2SO_3)_3,13H_2O$; basic ferric *p*-dibromobenzenesulphonate, $Fe(OH)(C_6H_3Br_2SO_3)_2,12H_2O$; chromium *p*-dibromobenzenesulphonate, $Cr(C_6H_3Br_2SO_3)_3,14H_2O$; aluminium *p*-dibromobenzenesulphonate,
$$Al(C_6H_3Br_2SO_3)_3,18H_2O;$$
scandium *p*-dibromobenzenesulphonate, $Sc(C_6H_3Br_2SO_3)_3,14H_2O$, and
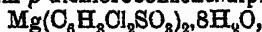
cobaltous p-dibromobenzenesulphonate, $Co(C_6H_3Br_2SO_3)_2,9H_2O$, have been prepared and described without crystallographic details. It is shown that similar conclusions may be drawn with regard to the structure of p-dichlorosulphonic acid as were drawn in the case of p-dibromosulphonic acid in the previous paper (*loc. cit.*). The structure of the sulphonates of monad and dyad metals is discussed ; it is argued that in the formation of the latter the molecules of benzene in contiguous rows become separated by the intervention of the sulphonic radicles which are united in pairs by the metallic atom. The structure of the salts containing monad metals appears in some cases to be pseudo-trigonal like that of the acid ; in others to resemble that of the dyad metals.   J. F. S.

p- and o-Toluenesulphinic Acids. ALFRED HEIDUSCHKA and HANS LANGKAMMERER (*J. pr. Chem.*, 1913, [ii], **88**, 425—442).—An extension of the work of E. von Meyer and others (A., 1901, i, 264 ; 1903, i, 808) on the formation of aminodiaryl sulphides by the inter· action of aromatic sulphinic acids and amines.

The authors find that the sulphides are obtained in a purer condition and better yield by fusing the sulphinic acids with the hydrochlorides of the amines, instead of with the free bases.

When p-toluenesulphinic acid is fused at 215° with aniline hydrochloride and the product extracted with ether, p-*aminophenyl* p-*tolyl sulphide* p-*toluenesulphonate*, $C_{20}H_{21}O_3NS_2$, is obtained in white needles, m. p. 216° ; extraction of the residue with hydrochloric acid yields the corresponding *hydrochloride*.

p-Aminophenyl p-tolyl sulphide condenses with 4-bromo-2-hydroxybenzaldehyde in boiling alcoholic solution to form p-4-*bromo-2-hydroxybenzylideneaminophenyl* p-*tolyl sulphide*,

$$C_6H_4Me·S·C_6H_4·N:CH·C_6H_3Br·OH,$$
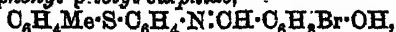
which crystallises in lustrous, brownish-yellow leaflets, m. p. 148° ; the m-*xylylidene* derivative, $C_6H_4(CH:N·C_6H_4·S·C_6H_4Me)_2$, from m-phthalaldehyde, has m. p. 163°.

The *benzylidene* derivative, $C_6H_4Me·S·C_6H_4·N:CHPh$, is obtained in the form of its *hydrochloride* (yellow needles, m. p. 164°, which rapidly acquire a greenish colour) by condensing benzaldehyde with p-aminophenyl p-tolyl sulphide hydrochloride ; the *hydrochlorides* of the *salicylidene* and *vanillylidene* derivatives have m. p. 175° and 195° respectively.

The aqueous extract of the product obtained by fusing o-anisidine hydrochloride with p-toluenesulphinic acid at 225° yields o-*anisidine* p-*toluenesulphonate*, $C_{14}H_{17}O_4NS$, which has m. p. 150°, and has also been prepared directly from its components in alcoholic solution ; extraction of the product with hydrochloric acid yields 4-*amino-3-methoxyphenyl* p-*tolyl sulphide hydrochloride*,.

$$C_6H_4Me·S·C_6H_3(OMe)·NH_2,HCl.$$
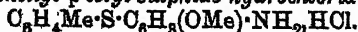
This has m. p. 215°, and on treatment with aqueous ammonia yields the free *base*, which, however, could not be obtained in a pure condition. The free base combines with phenylcarbimide in ethereal solution to form the *carbamide*, m. p. 163°,
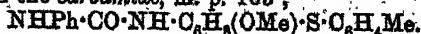
$$NHPh·CO·NH·C_6H_3(OMe)·S·C_6H_4Me.$$

o-*Anisidine* p-*toluenesulphinate*, prepared from its components in alcoholic solution, has m. p. 112°. o-*Chloroaniline* p-*toluenesulphonate*, m. p. 198°, and o-*chloroaniline* p-*toluenesulphinate*, m. p. 130°, were prepared in a similar manner.

3-*Chloro*-4-*aminophenyl* p-*tolyl sulphide hydrochloride*,

$$C_6H_4Me·S·C_6H_3Cl·NH_2,HCl,$$
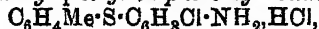
obtained by fusing p-toluenesulphinic acid with o-chloroaniline hydrochloride, forms colourless crystals, m. p. 150°, and on treatment with aqueous ammonia yields the free *base*, which combines with phenylcarbimide in ethereal solution to form the *carbamide*,

$$NHPh·CO·NH·C_6H_3Cl·S·C_6H_4Me,$$
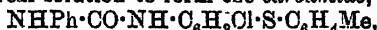
crystallising in white needles, m. p. 190°; the corresponding *thiocarbamide* prepared in a similar manner has m. p. 147°.

p-*Aminophenyl* o-*tolyl sulphide*, $NH_2·C_6H_4·S·C_6H_4Me$, obtained in the form of its o-*toluenesulphonate*, $C_{20}H_{21}O_3NS_2$, m. p. 190°, by fusing aniline hydrochloride with o-toluenesulphinic acid and extracting the product with water, separates from ether in flat, hexagonal, brown pyramids, m. p. 50°, forms a *hydrochloride*, crystallising in slender, white needles, m. p. 137°, and condenses with benzaldehyde in alcoholic solution, yielding the *benzylidene* derivative, which was isolated in the form of its *hydrochloride*, $C_6H_4Me·S·C_6H_4·N:CHPh,HCl$, as a yellow powder, m. p. 195°. It combines with phenylcarbimide in ethereal solution yielding the *carbamide*, $NHPh·CO·NH·C_6H_4·S·C_6H_4Me$, crystallising in white needles, m. p. 164°. **F. B.**

Electrochemical Reduction of Organic Halogen Compounds. II. Kurt Brand (*Ber.*, 1913, **46**, 2935—2942).—This and the succeeding paper give the results of attempts to reproduce by electrochemical methods the conversion of diaryltrichloroethanes into stilbene derivatives, first effected by chemical methods by Goldschmidt, and later by Elbs (Abstr., 1893, i, 271). The results show that the products obtained depend in part on the nature of the cathode used. The apparatus used is described. The cathode liquid, which was kept boiling, consisted of the substance under examination in alcohol and hydrochloric acid.

Lead cathode.—ββ β-Trichloro-aa-diphenylethane yielded stilbene (4% of the theoretical) and dichlorodiphenylethane. ββ β-Trichloro-aa-di-p-tolylethane gave 6% of the theoretical yield of p : p′-dimethylstilbene. ββ β-Trichloro-aa-di-p-anisylethane gave about 10% of the calculated yield of p : p′-dimethoxystilbene, and a similar yield of p : p′-diethoxystilbene was obtained from ββ β-trichloro-aa-di-p-phenetylethane. These alkylstilbenes were identified by means of their dibromides.

Copper cathode.—The four diaryltrichloroethanes mentioned in the preceding paragraph were also submitted to electrolytic reduction in presence of a copper cathode, and then yielded the corresponding diaryldichloroethanes, but the first-named product gave only a small yield. The last-named substance also yielded a minute amount of the corresponding diethoxystilbene. The diaryldichloroethanes were identified by conversion into the corresponding ethylenes, which give characteristic colours with sulphuric acid. **T. A. H.**

**Electrochemical Reduction of Organic Halogen Compounds.
III.** KURT BRAND and M. MATSUI (*Ber.*, 1913, **46**, 2942—2951).
—It has been shown previously (Brand, *Zeitsch. Elektrochem.*, 1910,
16, 669) that the principal product of the electrolytic reduction of
hot alcoholic solutions of $\beta\beta\beta$-trichloro-aa-diphenylethane in presence
of a lead cathode is a hydrocarbon, $C_{26}H_{22}$, which may have the con-
stitution $CHPh_2 \cdot C \vdots C \cdot CHPh_2$ or $CPh_2 \vdots C \cdot CH \cdot CHPh_2$ (see also preceding
abstract). It is now shown that the cathodic reduction of $\beta\beta\beta$-tri-
chloro-aa-di-p-tolylethane and of di-$\beta\beta\beta$-trichloro-aa-di-p-anisyl-ethane
under analogous conditions furnishes similar substances, some reactions
of which are described. These reactions do not enable a final
decision as to the constitution to be arrived at, but on the whole they
tend to support formulæ of the kind represented by the second given
above.

$\beta\beta\beta$-Trichloro-aa di-p-tolylethane furnishes the *hydrocarbon*, $C_{32}H_{30}$,
m. p. 123°, which crystallises from boiling alcohol in colourless, small
needles, shows a faint blue fluorescence, and on oxidation in acetone
solution with potassium permanganate yields di-p-tolylacetic acid and
di-p-tolyl ketone; the same products are formed with calcium perman-
ganate in presence of pyridine, and with chromic acid in acetic acid, but
in different amounts. On reduction with excess of sodium in amyl
alcohol, the hydrocarbon yields the corresponding *tetra*-p-*tolylbutane*,
m. p. 126°, crystallising from alcohol in colourless needles showing a
slight blue fluorescence. With insufficient sodium, a *substance*, m. p.
186°, crystallising in glancing leaflets, is formed in small quantity.
With sodium in absolute alcohol, the same reduction takes place. On
treatment with sodium ethoxide in alcohol, the hydrocarbon is con-
verted into $aa\delta\delta$-*tetra*-p-*tolyl*-$\Delta^{a\gamma}$-*butadiene*,

$$C(C_6H_4Me)_2 \vdots CH \cdot CH \vdots C(C_6H_4Me)_2,$$
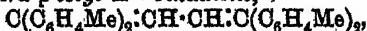
m. p. 255°, which crystallises from methyl ethyl ketone in heavy,
green, fluorescent needles, is sparingly soluble in boiling alcohol, but
readily so in chloroform or benzene, giving solutions which are green in
colour and show absorption in the extreme violet end of the spectrum.
The hydrocarbon, $C_{32}H_{30}$, reacts with mercuric acetate to form an
orange-yellow *compound* of uncertain composition, which with hydrogen
chloride or with zinc and acetic acid yields the tetratolylbutadiene
described above.

Di-p-anisyltrichloroethane yields in addition to di-p-methoxystilbene
(preceding abstract) the *phenol ether*, $C_{32}H_{30}O_4$, which, as indicated
above, is probably $aa\delta\delta$-tetra-p-anisyl-$\Delta^{a\beta}$-butadiene,

$$(C_6H_4 \cdot OMe)_2 C \vdots C \cdot CH \cdot CH(C_6H_4 \cdot OMe)_2.$$
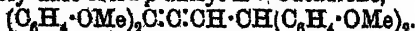
It melts at 111°, crystallises from boiling alcohol in colourless needles,
and on oxidation with chromic acid gives di-p-anisyl ketone and a
small amount of di-p-anisylacetic acid. On reduction with sodium
in amyl alcohol, $aa\delta\delta$-*tetra*-p-*anisylbutane*, m. p. 116°, crystallising
in colourless needles with a blue fluorescence, is formed, whilst
with sodium ethoxide in alcohol, $aa\delta\delta$-*tetra*-p-*anisyl*-$\Delta^{a\gamma}$-*butadiene*,
m. p. 149°, which crystallises from methyl ethyl ketone in green,
fluorescent needles, is produced. These two substances closely
resemble their analogues described in the preceding paragraph.

                                                    T. A. H.

Dehydrobenzylidenebisfluorene. ROBERT STOLLÉ (*Ber.*, 1913, 46, 2979).—In preparing benzoylfluorene by Werner's method (A., 1906, i, 436), but using potassium ethoxide instead of sodium, the author has obtained a small quantity of *dehydrobenzylidenebisfluorene*, $C_{32}H_{22}$, m. p. 350°, which crystallises from chloroform in small, orange needles, and on heating sublimes to form red crystals. It is hardly soluble in ether or alcohol, and sparingly soluble in hot benzene or acetic acid. The analogous ethylidene compound has been described by Pummerer and Dorfmüller (this vol., i, 963).   T. A. H.

Studies in the Fluorene Series. FRITZ MAYER (*Ber.*, 1913, 46, 2579—2587).—The author has attempted to synthesise fluoranthene by the ring condensation of 9-ethylfluorene, fluorene-9-acetic acid or fluorenepropionic acid, but without success. On heating distilled ethylfluorene with litharge and distilling the product, 9-ethylidene-fluorene, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!>\!C{:}CHMe$ (Ullmann, A., 1906, i, 77), which formed a picrate, m. p. 156°, was obtained. When crude ethylfluorene was employed, however, and the product was not distilled, a 9-fluorene-ethyl alcohol, which also gave a picrate, m. p. 155—156°, was formed. It was not identical with Ullmann's carbinol (*ibid.*) and has therefore the constitution $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!>\!CH{\cdot}CH(OH)Me$ or $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!>\!CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$. In each case, very small quantities of high-melting, red hydrocarbons of the formula $C_{15}H_{10}$ were obtained. It was expected that one of them would be identical with the compound,

$$\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!>\!CH{\cdot}CH{:}C\!<\!\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix},$$
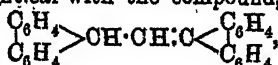
described by Wislicenus and Densch (A., 1902, i, 291), but the author could not prepare this substance by any means.

Twenty grams of crude 9-ethylfluorene, from the action of ethyl iodide on ethyl fluorene-9-oxalate (*loc. cit.*), were heated for fifteen minutes at 310—360° with 40 grams of litharge, when the product was extracted with boiling chloroform. The solvent deposited a red *hydrocarbon*, $C_{15}H_{10}$ or $C_{27}H_{18}$, m. p. over 360°, on cooling, and the dark brown *picrate* of a fluorene-ethyl alcohol, $C_{21}H_{17}O_8N_3$, m. p. 155—156°, was obtained from the mother liquor. The *picrate* of Ullmann's carbinol has the same m. p., but not so a mixture of the two.

Two parts of distilled 9-ethylfluorene, b. p. 306—310°, were heated with five parts of litharge for one hour, the product was extracted with hot chloroform, which deposited a red *hydrocarbon*, $(C_{15}H_{10})x$, m. p. 300—310°, and the residue, after evaporating the solvent, was distilled. The fraction, b. p. 310—320°, contained ethylidenefluorene and formed a *picrate*, $C_{21}H_{15}O_7N_3$, m. p. 155—156°.

For the preparation of *fluorene-9-acetic acid*, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!>\!CH{\cdot}CH_2{\cdot}CO_2H$, ethyl fluorene-9-oxalate was treated with sodium in alcohol and ethyl bromoacetate, and the product was hydrolysed by 20% aqueous sodium hydroxide. The acid has m. p. 129—130°, forms a *methyl* ester,

$C_{16}H_{14}O_2$, m. p. 60°, an *amide*, $C_{15}H_{13}ON$, slender needles, m. p. 189°, and yields 9-methylfluorene (*ibid.*) on distillation with soda-lime. *Fluorene-9-propionic acid*, $C_{16}H_{14}O_2$, was also prepared, using ethyl β-iodopropionate; it forms white needles, m. p. 144°. Neither the acids themselves nor their chlorides gave definite products on condensation.   J. C. W.

Tri-β-naphthylmethane and Certain of its Derivatives. ALEXEI E. TSCHITSCHIBABIN and S. I. KOBJAGIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 766—781 ; *J. pr. Chem.*, 1913, [ii], **88**, 505—578).— Tri-β-naphthylcarbinol (compare Schmidlin and Huber, A., 1910, i, 832) may be readily obtained by the interaction of di-β-naphthyl ketone and magnesium β-naphthyl bromide (see A., 1911, i, 969) in presence of ether.

The authors were unable to prepare 2-bromonaphthalene by Darzens and Berger's method (A., 1909, i, 297), but obtained it readily from β-naphthylamine by passing through the diazo-compound.

Di-β-naphthyl ketone (compare Grucarevic and Merz, A., 1873, 263, 264) was prepared by the dry distillation of calcium β naphthoate, by oxidising di-β-naphthylcarbinol by the action of β-naphthoyl chloride on naphthalene in presence of zinc and by the action of magnesium β-naphthyl bromide on β-naphthoyl chloride. The first method gives poor, and the last good yields.

Tri-β-naphthylcarbinol, $C_{31}H_{22}O$, forms snow-white crystals, m. p. 204°, and dissolves in concentrated sulphuric acid with an intense coloration, which is greenish in thin layers or low concentrations, and violet-red when more concentrated. These solutions show an absorption band gradually weakening from the violet to the blue, with a maximum intensity at about 490 μμ, and also a faint band in the red, beginning at about 755 μμ. Unlike the isomeric tri-α-naphthyl-carbinol (A., 1911, i, 969), it shows no inclination to oxidise in the air. *Tri-β-naphthylchloromethane*, $C_{31}H_{21}Cl$, forms white crystals, m. p. 199—201° (decomp.), the fused mass solidifying later, and then showing m. p. 231—236° ; with sulphuric acid it gives the same coloration as the carbinol.

Tri-β-naphthylmethane, $C_{31}H_{22}$, prepared by reducing the above carbinol or chloride by means of hydriodic and glacial acetic acids (A., 1911, i, 277), forms colourless, prismatic crystals, m. p. 178—179°, and exhibits the normal molecular weight in freezing benzene. When crystallised from benzene, it yields crystals containing varying proportions of benzene, possibly owing to the formation of a solid solution.

β-Naphthyldi-ββ-naphthafluorene, $C_{31}H_{20}$, obtained on reduction of the impure tri-β-naphthylchloromethane or by heating the latter above its melting point in an atmosphere of carbon dioxide, forms white, nodular crystals, which melt at 235—237° in a sealed capillary filled with carbon dioxide. Its solutions exhibit intense blue fluorescence and react with magnesium methyl iodide with evolution of methane.

The action of copper-bronze or of Gomberg and Cone's molecular silver (A., 1906, i, 822) on a solution of tri-β-naphthyl-

chloromethane yields a dark violet-red liquid from which dark violet crystals were separated. These have not been analysed, but from their colour and ready oxidisability in the air, and the molecular weights indicated by cryoscopic measurements in benzene and naphthalene, it seems probable that they consist principally of *tri-β-naphthylmethyl*, $C(C_{10}H_7)_3$, and to a small extent of hexa-β-naphthylethane. T. H. P.

Phenyldichloroamine [Di-ω-chloroaniline]. STEFAN GOLD-SCHMIDT (*Ber.*, 1913, **46**, 2728—2736).—The existence of di-ω-chloroaniline and ω-chloroaniline as intermediate products in the action of hypochlorites on aniline has already been indicated by Raschig (*Zeitsch. angew. Chem.*, 1907, **20**, 2065; compare also Bamberger, A., 1894, i, 238).

The dichloro-compound has now been isolated by the author by the interaction of aniline and hypochlorous acid in ethereal solution at a low temperature. The ethereal solution of hypochlorous acid is obtained by extracting an aqueous solution of the acid, prepared according to Wohl's method (A., 1907, i, 194), with ether, and rapidly cooling to $-15°$. At the ordinary temperature the solution is unstable and rapidly decomposes, yielding acetaldehyde and hydrogen chloride.

When treated with slightly less than the calculated amount of aniline in ethereal solution at $-15°$ to $-20°$, a yellow solution is obtained, which on evaporation at $-40°$ yields *di-ω-chloroaniline*, $NPhCl_2$, as a viscid oil, having a colour similar to that of potassium dichromate. Although in the free condition, the dichloroamine is very unstable and decomposes explosively when removed from the freezing mixture; in ethereal solution it may be kept for several hours without undergoing appreciable change. It liberates iodine from potassium iodide, and on treatment with ethereal hydrogen chloride rapidly decomposes, with the formation of 2:4-dichloroaniline and 2:4:6-trichloroaniline.

When treated with sodium hydroxide, alcoholic ammonia, sodium thiosulphate, aniline or copper powder, it yields *p*-aminodiphenylamine hydrazobenzene and benzoquinonephenyldi-imine; it is probable that the free radicle NPh: is formed as an intermediate product in these decompositions.

Attempts to prepare ω-chloroaniline by the interaction of molecular quantities of aniline and hypochlorous acid in ethereal solution at a low temperature were unsuccessful.

ωω-2:4:6-Pentachloroaniline, prepared from 2:4:6-trichloroaniline and hypochlorous acid in a similar manner to that described above for the preparation of di-ω-chloroaniline, is much more stable than the latter compound, and forms a viscid oil having the colour of diphenylketen. It has a sweet, disagreeable odour resembling that of chlorine, and solidifies at $-80°$ to a glassy mass. When heated, it becomes dark in colour and decomposes explosively with the production of flame. It dissolves in strong sulphuric acid, yielding violet solutions, which become yellow and evolve chlorine, when warmed.

On the addition of potassium iodide in aqueous alcoholic solution to an ethereal solution of the dichloro-compound, iodine (2 atoms) is liberated and $2:4:6:2':4':6'$--hexachloroazobenzene is formed; in the presence of hydrochloric acid, $2:4:6$-trichloroaniline is produced, the amount of iodine liberated in this case being twice that given above.

A sketch of the apparatus employed in the preparation of the dichloroamines is given.   F. B.

A New Group of Metallic Compounds of the Aromatic Thiocarbamide Series. RUDOLF KRULLA (*Ber.*, 1913, **46**, 2669—2672).—Aryl thiocarbamides are readily prepared by the action of aryl amines on carbon disulphide in the presence of a substance which absorbs the liberated hydrogen sulphide. For this purpose, the author recommends nitrobenzene, which reacts in accordance with the equation : $5NH_2Ph + 3CS_2 + Ph \cdot NO_2 = 3(PhNH)_2CS + 2H_2O + 3S$. He has also employed a number of metallic oxides and salts for this purpose, and thus obtained a new series of organometallic derivatives, of which the *tin* compounds have been most completely investigated.

When an alcoholic solution of aniline and carbon disulphide is treated with tin hydroxide, a yellow tin salt, $Sn(S \cdot CS \cdot NHPh)_2$, is immediately precipitated in a practically pure condition. Like the similar salts of other metals, it is almost insoluble in most solvents except acetone and a mixture of acetone and alcohol, and is readily decomposed when warmed, even in solution. Warm acids immediately convert it into diphenylthiocarbamide and the corresponding metallic salt, whilst prolonged contact with aniline causes a similar change. Lead hydroxide similarly yields a *lead* salt, fine needles, when added to a dilute alcoholic solution of aniline and carbon disulphide ; in concentrated solution, however, a dark green coloration is observed, and hydrogen sulphide is evolved with perceptible heat evolution. This appears to be the only case in which hydrogen sulphide is given off.

The *bismuth* salt forms long needles, readily soluble in alcohol.

In the cases of arsenic and antimony, the organometallic derivatives could not be isolated, the thiocarbamide and the metallic sulphide being the products of the action. Copper behaved similarly to the alkali metals, forming xanthates.

Homologues of aniline which do not contain too many acidic groups react analogously. In these cases it often occurs that lead oxide or hydroxide is active when tin is no longer useful. Organometallic derivatives have been obtained from *p*-toluidine, monomethylaniline, *p*-aminophenol, *a*- and *β*-naphthylamine. Diphenylamine did not react.   H. W.

New Methods of Preparing Thiocarbanilides. HARRY S. FRY (*J. Amer. Chem. Soc.*, 1913, **35**, 1539—1546).—The method of preparing thiocarbanilides by the interaction of carbon disulphide and an aromatic amine frequently fails in its desired object, and the cause is attributed to the alcohol and potassium hydroxide which are generally introduced into the reaction mixture. By omitting the

alcohol and replacing the alkali by pyridine, the process is so improved that a better yield of a purer product is just as readily obtained. A specimen of di-o-chlorophenylthiocarbamide prepared in this manner had m. p. 130·5° (compare Grosch, A., 1899, i, 599).

By applying iodine together with pyridine, the former to remove the hydrogen sulphide from the primary reaction and the latter to combine with the hydriodic acid formed in the secondary reaction of the hydrogen sulphide, excellent yields of the various thiocarbanilide compounds can be obtained; the process in this respect is greatly superior to the previous one. The reaction may be summed up by the equation: $2NH_2R + CS_2 + I_2 + 2C_5H_5N = CS(NHR)_2 + 2C_5H_5N,HI + S$. An excess of carbon disulphide is applied (both in this and in the previous method), and during the action which occurs without warming, pyridine hydriodide separates. The reaction product is steam distilled, and the mixture of thiocarbanilide and sulphur obtained by filtration of the aqueous residue is then separated by extraction with alcohol.

In the preparation by the latter process with iodine it is important that only the theoretical proportions of aniline and iodine should be used. With excess of iodine, the reaction proceeds quantitatively to the formation of a thiocarbimide according to the equation: $NH_2R + CS_2 + I_2 + 2C_5H_5N = RNCS + 2C_5H_5N,HI + S$. Indeed, this reaction provides a convenient method for the estimation of aniline (dissolved in a mixture of carbon disulphide and pyridine) by direct titration with a solution of iodine in carbon disulphide. D. F. T.

Transformation of Phenyl Allyl Ethers into the Isomeric Allylphenols. LUDWIG CLAISEN and OTTO EISLEB (*Annalen*, 1913, 401, 21—119).—It has been shown (A., 1912, i, 965) that the allyl ethers of several phenols change almost quantitatively by heating, sometimes even below the b. p., to the isomeric allylphenols. In order to test the generality of the change, a large number of aromatic allyl ethers have been examined; all without exception undergo the change.

The ethers are of the types (i) R⟨◯⟩$O·C_3H_5$, (ii) ⟨◯⟩$O·C_3H_5$ with R, R,

and (iii) ⟨◯⟩$O·C_3H_5$ with R. Those of type (i) change very easily to o-allylphenols, and those of type (ii) readily to p-allylphenols. Ethers of type (iii) yield o-allylphenols, so the allyl group preferentially enters the nucleus in the ortho-position to the hydroxyl group. The b. p.'s /0 mm. of the allylphenols and also the densities are generally higher than the corresponding constants of the isomeric allyl ethers; exceptions, however, are the allyl ethers of phenols containing a negative substituent in the ortho-position to the hydroxyl group, the b. p.'s of these being higher than the b. p.'s of the isomeric allylphenols.

With suitable ethers changes such as:

$(o)OMe·C_6H_4·O·C_3H_5 \longrightarrow OMe·C_6H_3(C_3H_5)·OH \longrightarrow$
$OMe·C_6H_3(C_3H_5)·O·C_3H_5 \longrightarrow OMe·C_6H_2(C_3H_5)_2·OH$
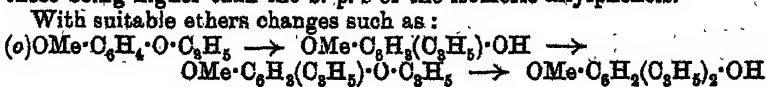
proceed with good yields. Such changes occur particularly easily with allyl ethers of phenolaldehydes and phenolcarboxylic acids and their esters. However, when the aldehyde or carboxyl group occupies a position in the nucleus into which the allyl group desires to enter, it is eliminated as carbon monoxide or carbon dioxide respectively; for example, by alternate heating and allylation, esters of *o*-allyloxybenzoic acid are converted into 2-allyloxy-3 : 5-diallylbenzoates ; the latter then change to 2 : 4 : 6-triallylphenol by hydrolysis and heating.

In addition to the change to *o*-propenylphenols by heating with aqueous potassium hydroxide (*loc. cit.*), *o*-allylphenols are changed in another manner by heating with an acid catalyst, such as pyridine hydrochloride ; this change, whereby dihydrocoumarones are produced,

$$\text{OH·C}_6\text{H}_4\text{·CH}_2\text{·CH:CH}_2 \;\rightarrow\; \text{C}_6\text{H}_4\overset{\text{CH}_2}{\underset{\text{O}}{<}}\text{>CHMe, will be described}$$

in a future communication.

The aromatic allyl ethers described below are prepared generally by boiling the phenol in acetone with allyl bromide and finely powdered potassium carbonate. For the preparation of the allyl bromide, Merling and Jacobi's hydrogen bromide method (A., 1894, i, 162) is recommended, the yield being 85%. An apparatus is figured and described by which 120—150 grams of hydrogen bromide per hour can be obtained quantitatively from its elements.

Although the change frequently occurs at lower temperatures, the optimum temperature, at which the change is complete usually in a few seconds or minutes, for the conversion of the aromatic allyl ether into the allylphenol is 230—250°. Difficultly volatile phenyl allyl ethers cannot have a b. p. under ordinary pressures, because they change to the allylphenol before the b. p. is reached.

p-*Chlorophenyl allyl ether*, $\text{C}_6\text{H}_4\text{Cl·O·C}_3\text{H}_5)$, b. p. 106—107°/12 mm., D^{15} 1·131, a colourless liquid having an odour of aniseed, is converted by boiling for twenty to twenty-five minutes into 4-*chloro-2-allylphenol*, $\text{OH·C}_6\text{H}_3\text{Cl·C}_3\text{H}_5$, m. p. 48°, b. p. 256—260° or 124—125°/12 mm., D^{15} 1·171 (supercooled liquid), which develops an olive-green coloration with alcoholic ferric chloride and forms a p-*nitrobenzoate*, m. p. 82°. p-*Bromophenyl allyl ether*, b. p. 126°/14 mm., yields by boiling for a few minutes 4-*bromo-2-allylphenol*, m. p. 50°, b. p. 274—280° or 142—144°/14 mm. p-*Nitrophenyl allyl ether*, m. p. 18·5°, b. p. 160°/12 mm., faintly yellow prisms, yields about 40% of 4-*nitro-2-allylphenol* at 260°; the latter has m. p. 79°, b. p. 190°/11 mm., and crystallises in colourless leaflets. p-*Benzeneazophenyl allyl ether*,

$$\text{C}_6\text{H}_5\text{·N}_2\text{·C}_6\text{H}_4\text{·O·C}_3\text{H}_5,$$

m. p. 52°, yellowish-red needles and prisms, yields by heating in petroleum at 230° about 70% of o-*allylbenzeneazophenol*, m. p. 97—98°, yellow needles and prisms (*benzoate*, m. p. 92°, brownish-red crystals).

p-*Tolyl allyl ether*, b. p. 211—213° or 91°/12 mm., D^{15} 0·967, yields by boiling for one hour 3-*allyl-p-cresol*, b. p. 236—238° or 112°/12 mm., D^{15} 1·006 (p-*nitrobenzoate*, m. p. 69°). By heating with potassium hydroxide and water at 140—145°, 3-allyl-p-cresol is converted into 3-*propenyl-p-cresol*, b. p. 120—124°/11 mm., the *methyl ether* of which is oxidised to 4-*methoxyisophthalic acid* by potassium permanganate. By allylation, 3-allyl-p-cresol yields 3-*allyl-p-tolyl allyl ether*, b. p.

123—127°/14 mm., from which is obtained by prolonged heating a very small quantity of a *substance*, b. p. 135—145°/14 mm., which is possibly 4-*methyl*-3 : 5-*diallylphenol*.

Eugenyl allyl ether, b. p. 140°/9 mm., D^{15} 1·024, changes very easily at 230° to o-*allyleugenol*, b. p. 285—287° or 149°/10 mm., D^{15} 1·036, which develops a deep blue to deep green coloration with alcoholic ferric chloride and forms a p-*nitrobenzoate*, m. p. 136°.

The eugenol obtained previously (*loc. cit.*) by the transformation of guaiacyl allyl ether is now definitely proved to be o-eugenol (o-allyl-guaiacol), since it yields by treatment with aqueous potassium hydroxide at 170° a propenylguaiacol, m. p. 78°, which is identical with Pauly and Buttlar's o-*isoeugenol*, (A., 1911, i, 785). o-*Eugenyl allyl ether*, b. p. 128°/10 mm., D^{15} 1·016, changes at 200° to o-allyleugenol, identical with the substance obtained by the transformation of eugenyl allyl ether.

o-*Tolyl allyl ether*, b. p. 205—208° or 85°/12 mm., D^{15} 0·969, is changed by boiling to 2-*methyl*-3-*allylphenol*, b. p. 231—233° or 106—107°/12 mm., D^{15} 1·007, which must contain the allyl group in the ortho-position to the hydroxyl group, since it is also obtained by heating 2-allyloxy-m-toluic acid (see below).

m-*Tolyl allyl ether*, b. p. 211—214° or 92—94°/12 mm., D^{15} 0·965, is changed by boiling to 3-*methyl*-2(or 4)-*allylphenol*, b. p. 239—240° or 111—112°/11 mm., D^{15} 1·012; since the liquid has been separated into a liquid and a solid, m. p. 53°, possibly both allyl-m-cresols are present in it. By further allylation it yields *allyl*-m-*tolyl allyl ether*, which changes at 230° to 3-*methyl*-2 : 4-*diallylphenol*, b. p. 272—274° or 140°/15 mm., to the extent of about 30%.

o-*Nitrophenyl allyl ether*, b. p. 155°/12 mm., is changed by heating at 180° for five hours to 6(?)-*allyl-o-nitrophenol*, m. p. 9°, b. p. 130—135°/15 mm. (*barium* salt, golden-red leaflets).

α-*Naphthyl allyl ether* is an oil which cannot be distilled, even under diminished pressure, without partly changing to 2-*allyl-α-naphthol*, b. p. 171°/12 mm. (p-*nitrobenzoate*, m. p. 99°). The allylnaphthol, which is obtained in 50—60% yield at 230°, condenses with benzenediazonium chloride to form 4-*benzeneazo*-2-*allyl-α-naphthol*, m. p. 157—158°, red crystals with green reflex.

The behaviour of ethyl o-allyloxybenzoate has been recorded (*loc. cit.*). The position of the allyl group in the transformed product is proved by elimination of the carbethoxy group, whereby o-allylphenol is obtained. *Methyl o-allyloxybenzoate*, b. p. 143°/12 mm., D^{15} 1·118, changes by heating to *methyl* 3-*allylsalicylate*, b. p. 130°/10 mm., D^{15} 1·120°, with almost explosive violence; the latter gives a bluish-violet coloration with alcoholic ferric chloride, and yields 3-*allylsalicyl-amide*, $C_3H_5 \cdot C_6H_3(OH) \cdot CO \cdot NH_2$, m. p. 99°, colourless plates, by prolonged keeping with concentrated methyl-alcoholic ammonia. By heating 2-allyloxybenzoic acid, the allyl does not displace the carboxyl group as in the cases recorded below, but enters position 3, as is proved by the conversion of the resulting 3-allylsalicylic acid into o-allylphenol at 300°. o-Allylphenol condenses with benzenediazonium chloride to form the benzeneazo-o-allylphenol mentioned above. 2-*Methoxy*-3-*allylbenzoic acid*, m. p. 53°, is obtained by hydrolysing

the methyl ester, and 2-*acetoxy-3-allylbenzoic acid*,

$$C_8H_5 \cdot C_6H_3(OAc) \cdot CO_2H,$$
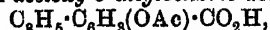
m. p. 96°, colourless needles, by boiling 3-allylsalicylic acid with acetic anhydride and potassium acetate.

Methyl 2-allyloxy-3-allylbenzoate, b. p. 152—162°/9 mm., obtained by heating methyl 3-allylsalicylate with allyl bromide and methyl alcoholic sodium methoxide, yields 2-*allyloxy-3-allylbenzoic acid*, m. p. 57°, by hydrolysis. By heating at about 250—260°, the acid is converted into 3 : 5-*diallylsalicylic acid*, m. p. 99°, and 2 : 6-*diallylphenol*, b. p. 256—258°, whilst the methyl ester yields *methyl* 3 : 5-*diallylsalicylate*, b. p. 155—165°/9 mm., which develops a dark blue coloration with ferric chloride. 3 : 5-*Diallylsalicylic acid*, m. p. 99°, colourless needles, gives an indigo blue colour with ferric chloride, and forms an *acetyl* derivative, m. p. 94°.

The allylation of methyl 3 : 5-diallylsalicylate yields *methyl* 2-*allyloxy-3 : 5-diallylbenzoate*, b. p. 180—182°/10 mm. This ester decomposes completely by heating under ordinary pressure, but the corresponding *acid*, m. p. 55°, is converted into 2 : 4 : 6-*triallylphenol*, b. p. 293—295° or 152—153°/10 mm., D^{15} 0·978 (*phenylcarbamate*, m. p. 97°).

Methyl 2-allyloxy-3-methylbenzoate, b. p. 130—140°/10 mm., is converted by heating into *methyl* 2-*hydroxy-3-methyl-5-allylbenzoate*, b. p. 275—290°, whilst 2-*allyloxy-3-methylbenzoic acid*, m. p. 59°, yields chiefly 2-*methyl-3-allylphenol*, b. p. 231—233°, 2-*hydroxy-3-methyl-5-allylbenzoic acid*, m. p. 127—129°, being obtained as a by-product.

Ethyl p-*allyloxybenzoate*, b. p. 156°/10 mm., is changed at 220—250° to *ethyl 4-hydroxy-3-allylbenzoate*, m. p. 78°, b. p. 185°/9 mm., the hydrolysis of which yields 4-*hydroxy-3-allylbenzoic acid*, m. p. 128°.

4-*Allyloxybenzoic acid*, m. p. 162°, crystallises in colourless plates and leaflets. By heating with concentrated aqueous potassium hydroxide at 180°, 4-hydroxy-3-allylbenzoic acid is converted into 4-*hydroxy-3-propenylbenzoic acid*, m. p. 169°.

Ethyl 4-allyloxy-3-allylbenzoate, b. p. 176°/9 mm., obtained by the allylation of ethyl 4-hydroxy-3-allylbenzoate (corresponding acid, $C_{13}H_{14}O_3$, m. p. 140°), is easily converted into *ethyl 4-hydroxy-3 : 5-diallylbenzoate*, m. p. 94°, b. p. 184—194°/9 mm., at 220—230°. 4-*Hydroxy-3 : 5-diallylbenzoic acid* has m. p. 108°. By allylation its ester is converted into *ethyl 4-allyloxy-3 : 5-diallylbenzoate*, b. p. 190°/10 mm., which decomposes when heated under ordinary pressure; the *acid*, $C_{16}H_{18}O_3$, m. p. 97°, however, is converted into 2 : 4 : 6-triallylphenol quantitatively at 300°.

2-*Allyloxybenzaldehyde*, b. p. 130°/10 mm., D^{15} 1·094, obtained almost quantitatively by boiling salicylaldehyde with allyl bromide and potassium carbonate in absolute alcohol, changes at 220—230° to 3-*allylsalicylaldehyde*, b. p. 245·5—246° or 111°/11 mm., D^{15} 1·098, which develops a bluish-violet coloration with alcoholic ferric chloride, forms a *copper* salt, $Cu(C_{10}H_9O_2)_2$, m. p. 181°, olive-brown needles, and *ferric* salt, $Fe(C_{10}H_9O_2)_3$, m. p. 110—111°, black crystals, condenses with benzenediazonium chloride in alkaline solution to form *benzeneazo-3-allylsalicylaldehyde*, $C_6H_5N_2 \cdot C_6H_2(OH)(C_3H_5) \cdot CHO$, m. p. 71°, yellow needles or prisms, and forms an *aldoxime*,

$$C_3H_5 \cdot C_6H_3(OH) \cdot CH:NOH,$$
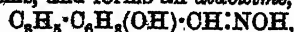
m. p. 79°. The oxime is converted by acetyl chloride into the *acetyl*

derivative, $C_3H_5 \cdot C_6H_3(OH) \cdot CH:NOAc$, m. p. 58° (from which the *nitrile* is obtained by heating), and the *hydrochloride*,

$$C_3H_5 \cdot C_6H_3(OH) \cdot CH:NOH, HCl.$$

By methylation by the potassium carbonate method, 3-allylsalicyl-aldehyde is converted into 2-*methoxy-3-allylbenzaldehyde*, b. p. 128°/9 mm., which is oxidised to 2-methoxy-3-allylbenzoic acid by alkaline hydrogen peroxide. The formation of this acid is the proof that the allyl group is in position 3 in the allylsalicylaldehyde obtained by the transformation of 2-allyloxybenzaldehyde.

2-*Allyloxy-3-allylbenzaldehyde*, b. p. 145—147°/11 mm., obtained by the allylation of 3-allylsalicylaldehyde, is converted at 200° into a 2 : 6-diallylphenol (75%) and 3 : 5-*diallylsalicylaldehyde*, b. p. 138—143°/10 mm. (*semicarbazone*, m. p. 154—156°). 2 : 6-Diallylphenol condenses with benzenediazonium chloride to form 4-*benzeneazo-2 : 6-diallylphenol*, m. p. 37°, reddish-yellow prisms.

2-*Allyloxybenzyl alcohol*, $C_3H_5O \cdot C_6H_4 \cdot CH_2 \cdot OH$, b. p. 133—150°/9 mm., obtained by the allylation of saligenin, yields formaldehyde and resinous products by heating.

4-*Allyloxybenzaldehyde*, b. p. 142°/10 mm., changes violently at 260—270°, and yields about 66% of 4-*hydroxy-3-allylbenzaldehyde*, m. p. 66°, b. p. 179°/9 mm. By allylation, the latter yields 4-*allyloxy-3-allylbenzaldehyde*, b. p. 164°/10 mm., which changes at 250° to 4-*hydroxy-3 : 5-diallylbenzaldehyde*, m. p. 67·5°, b. p. 185—190°/10 mm., to the extent of about 66%. This in its turn, by allylation, yields 4-*allyloxy-3 : 5-diallylbenzaldehyde*, which even by distillation under low pressures loses carbon monoxide and is converted into 2 : 4 : 6-triallylphenol.

The behaviour of 2-*allyloxy-3-methoxybenzaldehyde* (o-*vanillin allyl ether*), b. p. 156—160°/12 mm., obtained by the allylation of o-vanillin, is particularly interesting. By heating at 170—240°, it yields mainly o-eugenol, carbon monoxide being eliminated ; in addition, however, 2-*hydroxy-3-methoxy-5-allylbenzaldehyde* (5-*allyl-o-vanillin*), m. p. 48—49°, pale yellow crystals, and 4-*hydroxy-3-methoxy-5-allyl-benzaldehyde* (5-*allylvanillin*), m. p. 86°, b. p. 173°/9 mm., are formed. 5-Allyl-o-vanillin is almost odourless, develops a dark blue coloration with alcoholic ferric chloride, dissolves in 10% aqueous sodium carbonate, forms a *semicarbazone*, m. p. 195°, and in alcohol reacts with con-centrated aqueous ammonia to form an *imino*-derivative,

$$C_3H_5 \cdot C_6H_2(OMe)(OH) \cdot CH:NH,$$

m. p. 114°, yellow needles. By allylation, it is converted into 3-*methoxy-2-allyloxy-5-allylbenzaldehyde*, which changes at 170—285° into o-allyleugenol.

3-*Methoxy-4-allyloxybenzaldehyde* (p-*vanillin allyl ether*) changes very vigorously at ordinary pressure, and appreciably even at low pressures, to 5-allylvanillin ; at 210—220°, the yield is 80%. 3-*Methoxy-4-allyloxy-5-allylbenzaldehyde*, obtained by its further allylation, changes to o-allyleugenol by distillation, the amount of carbon monoxide evolved corresponding with an 82% yield. O. S.

Preparation of the Thymyl Ester of *iso*Valeryloxyacetic Acid. J. D. RIEDEL (D.R.-P. 260471. Compare this vol., i, 63).— *Thymyl chloroacetate*, a yellow oil, b. p. 262°, with a faint odour of thymol, is prepared by the condensation of thymol and chloroacetyl

chloride ; when treated with sodium *iso*valerate it furnishes *thymyl* iso-*valeryloxyacetate*, $C_6H_3MePr^\beta\cdot O\cdot CO\cdot CH_2\cdot O\cdot CO\cdot CH_2\cdot CHMe_2$, a yellow liquid, b. p. 207—209°/19 m.m., D 1·037, and of therapeutic value.

<div align="right">F. M. G. M.</div>

Action of Bromine and of Chlorine on Phenols. Substitution Products, ψ-Bromides, and ψ-Chlorides. XXVI. Action of Bromine on Di-*o*-cresoldimethylmethane [6 : 6'-Dihydroxy-ββ-di-*m*-tolylpropane]. THEODOR ZINCKE, J. KEMPF, and W. UNVERZAGT (*Annalen*, 1913, **400**, 27—47).—*m*- and *p*-Cresols condense with acetone in the presence of hydrogen chloride to form indifferent substances, $C_{20}H_{24}O_2$, which are probably ethers (Zincke and Gaebel, A., 1912, i, 442). *o*-Cresol (7 parts), acetone (1 part), and 0·7 part of hydrochloric acid, D 1·19, react at the ordinary temperature to form 6 : 6'-dihydroxy-ββ-di-*m*-tolylpropane,

$$CMe_2(C_6H_3Me\cdot OH)_2,$$

m. p. 136°, colourless needles, which is quite analogous to *pp*-dihydroxy-ββ-diphenylpropane (Zincke and Grüters, A., 1906, i, 172 ; Zincke, *ibid.*, i, 737) in its behaviour. It forms a *diacetyl* derivative, $C_{21}H_{24}O_4$, m. p. 88—89°, and reacts with bromine in cold glacial acetic acid to form 5 : 5'-*dibromo*-6 : 6'-*dihydroxy-ββ-di-*m*-tolylpropane*,

$$CMe_2(C_6H_2MeBr\cdot OH)_2,$$
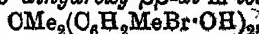
m. p 119—120°, colourless plates or double pyramids (*diacetyl* derivative, m. p. 145°). When treated in the cold with an excess of bromine without a solvent, dihydroxy-ββ-di-*m*-tolylpropane or the preceding dibromo-derivative yields 3 : 4 : 5-tribromo-*o*-cresol, tetrabromo-*o*-cresol (in one experiment a *substance*, $C_{10}H_6Br_5$, m. p. 250—251°), and ψ-3-*bromo-5-pentabromo*iso*propyl-o-cresol* (ψ-*hexabromo*-5-iso*propyl-o-cresol*), $OH\cdot C{<}^{CBr-CH}_{CMe\cdot CH}{>}C\cdot CBr(CHBr_2)_2$, m. p. 169—170° (decomp.), colourless, monoclinic prisms, which is insoluble in aqueous sodium hydroxide. The hexabromo-ψ-bromide resembles ψ-heptabromo-*p*-iso-propylphenol (Zincke and Grüters, *loc. cit.*) in its behaviour, and since the latter has the constitution $OH\cdot C_6H_2Br_2\cdot CBr(CHBr_2)_2$ (Zincke, A., 1912, i, 443), ψ-hexabromo-5-*iso*propyl-*o*-cresol probably has the constitution recorded above ; it certainly contains only one bromine atom in the benzene nucleus. It readily yields an *acetyl* derivative, $C_{12}H_{10}O_2Br_6$, m. p. 135—136°, stout plates, by treatment with acetic anhydride and concentrated sulphuric acid. By the action of alcohol and 2 *N*-sodium hydroxide at the ordinary temperature, the acetyl derivative is converted into 3-*bromo-5-tetrabromo*isopropenyl-o-cresol*, $OH\cdot C{<}^{CBr-CH}_{CMe\cdot CH}{>}C\cdot C(CHBr_2):CBr_2$, m. p. 94—95°, which forms an *acetyl* derivative, $C_{12}H_9O_2Br_5$, m. p. 114—115°, and *methyl ether*, $C_{11}H_9OBr_5$, m. p. 110—111°. By oxidation with boiling dilute nitric acid and silver nitrate, the methyl ether is converted into 3-*bromo*-2-*methoxy*-m-*toluic acid*, $C_9H_9O_3Br$, m. p. 206—207°, the formation of which proves the presence of only one bromine atom in the benzene nucleus of the methyl ether and, therefore, also in that of the hexabromo-ψ-bromide.

ψ-3-Bromo-5-pentabromo*iso*propyl-*o*-cresol, dissolved in acetone, is

converted by careful treatment with water at the ordinary temperature into 3-*bromo*-5-*tetrabromo*isopropylidenetoluquinone,

$$CO\overset{CBr=CH}{\underset{CMe:CH}{<}}>C:C(CHBr_2)_2,$$
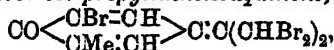
m. p. 180—181°, golden-yellow prisms, which is quite stable. It is reconverted into the hexabromo-ψ-bromide by hydrogen bromide in glacial acetic acid, yields a *diacetate*,

$$OAc\cdot C\overset{CBr-CH}{\underset{CMe:CH}{<}}>C\cdot C(CHBr_2)_2\cdot OAc,$$
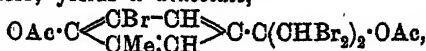
m. p. 160—161°, colourless needles, by treatment with acetic anhydride and concentrated sulphuric acid, and is converted into 3-*bromo*-5-*tetrabromomethoxy*isopropyl-o-*cresol*,

$$OH\cdot C\overset{CBr-CH}{\underset{CMe:CH}{<}}>C\cdot C(CHBr_2)_2\cdot OMe,$$
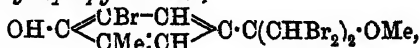
m. p. 100—101°, colourless prisms (*acetyl* derivative, $C_{18}H_{18}O_3Br_5$, m. p. 163°), by boiling methyl alcohol and a few drops of concentrated sulphuric acid.

The *phenol-alcohol*, $OH\cdot C\overset{CBr-CH}{\underset{CMe:CH}{<}}>C\cdot C(CHBr_2)_2\cdot OH$, m. p. 126°, colourless needles or prisms, corresponding with the preceding diacetate, cannot be prepared from the hexabromo-ψ-bromide or from the toluquinone by the addition of water, but is obtained from the latter in a curious manner by the action of glacial acetic acid and fuming sulphuric acid (20% SO_3) on the water-bath, water being subsequently added to the solution.

3-Bromo-5-tribromoisopropenyl-ᴏ-cresol is produced by the reduction of 3-bromo-5-tetrabromoisopropylidenetoluquinone by stannous chloride solution and hot glacial acetic acid, but has only been identified in the form of its *acetate*,

$$OAc\cdot C\overset{CBr-CH}{\underset{CMe:CH}{<}}>C\cdot C(CHBr_2):CHBr,$$
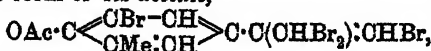
m. p. 90—91°, rhombic prisms or plates.

By shaking with aniline and glacial acetic acid, the hexabromo-ψ-bromide or the toluquinone is converted into *pentabromo*isopropyl-o-*cresol*-ψ-*anilide*, $C_{16}H_{14}ONBr_5$, m. p. 128—129°, which is given the quinonoid constitution, $CO\overset{CBr=CH}{\underset{CMe:CH}{<}}>CH\cdot C(CHBr_2)_2\cdot NHPh$, on account of its insolubility in alkalis. It forms colourless crystals which easily become yellow, and dissolves in boiling methyl or ethyl alcohol or glacial acetic acid; the yellow solutions deposit a *substance*, m. p. 223—224° (decomp.), intensely yellow prisms, which forms an orange-yellow *sodium* salt. The nature of the yellow substance has not yet been ascertained.　　　　　　　　　　　　　　　　　　　C. S.

[Preparation of Compounds containing Selenium.] August von Wassermann and Ernst Wassermann (D.R.-P. 261793).—When a solution of *p*-nitrosodimethylaniline in concentrated hydrochloric acid solution is treated with hydrogen selenide a bluish-red scum is formed; when this *leuco*-derivative (which was not isolated) is oxidised and subsequently treated with an aqueous solution of zinc chloride, a double

compound with zinc chloride is precipitated; this "selenoazine blue" is an analogue of methylene-blue, and can be employed as a dye and for the introduction of selenium into animal tissues; it forms a glistening, dark green bronze powder, readily soluble in water, sparingly so in alcohol.   F. M. G. M.

Action of Methyl Iodide on Aromatic Tellurides. KARL LEDERER (*Annalen*, 1913, **399**, 260—271).—Aromatic tellurides, unlike aromatic sulphides and selenides, readily react additively with methyl iodide, forming diarylmethyltelluronium iodides. From these, other salts can be prepared, specially characteristic being the sparingly soluble picrates, chromates, dichromates, and platinichlorides; the chlorides form double salts with the chlorides of mercury, gold, zinc, and copper.

The diarylmethyltelluronium hydroxides, prepared from the iodides by means of moist silver oxide, are extremely hygroscopic, oily liquids which have a strong alkaline reaction, liberate ammonia from its salts, precipitate the heavy metals in the form of their hydroxides, but do not combine with carbon dioxide. Aryl tellurides react with ethyl iodide only to a very small extent.

Phenyl telluride and methyl iodide, after being kept for two days, yield a crystalline *compound*, $TePh_2MeI,MeI$, which is converted by ether into *diphenylmethyltelluronium iodide*, $TePh_2MeI$, m. p. or decomp. 123—124° (bath at 110°), colourless needles (from hot water), which is decomposed by alcohol, as also are the *bromide*, m. p. 137—138°, small prisms, and *chloride*, m. p. 129—130° (decomp.). The *nitrate*, m. p. 168—169°, rhombic plates; *platinichloride*, m. p. 157—158°, microscopic, yellow plates; *chromate*, m. p. 151°, orange-red needles; *dichromate*, decomp. 153°, orange-red, quadratic leaflets; *picrate*, $C_{19}H_{15}O_7N_3Te,H_2O$, m. p. 93—94°, long, yellow needles; *mercurichloride*, $C_{13}H_{13}TeCl,HgCl_2$, m. p. 135—136°, colourless needles, and *zincichloride*, m. p. 149—150°, are described. *Diphenylmethyltelluronium hydroxide* has an odour of piperidine or pyrrolidine, and is decomposed by warm water.

p-Tolyl telluride and methyl iodide, after being kept for five days, yield, after treating the product with ether, *di-p-tolylmethyltelluronium iodide*, m. p. 85—86° (decomp.); the *picrate*, m. p. 157—158°, yellow needles; *mercurichloride*, m. p. 149—150° (decomp.); *chloride*, *bromide*, m. p. 73—74°; *dichromate*, m. p. 54—55°; *chromate*, m. p. 51—52°; *platinichloride*, m. p. 104—105°, and *aurichloride*, m. p. 35—36°, have been prepared, but the salts and also the *hydroxide* are not particularly stable, several of the preceding salts certainly being impure.

Di-o-tolylmethyltelluronium iodide, m. p. 125—126°, small crystals, is obtained directly from its components after keeping for fourteen days. The *bromide*, m. p. 134—135° (bath at 120°), small prisms; *nitrate*, m. p. 155—157°, hexagonal plates; *picrate*, m. p. 143—144°; *platinichloride*, m. p. 186°, microscopic, yellow prisms; *dichromate*, m. p. 171—172° (decomp.), orange-red needles; *chromate*, m. p. 161—162°, small, yellow prisms; *mercurichloride*, m. p. 134—135° (decomp.), felted needles, and basic *zincichloride*, $TeMe(C_7H_7)_2Cl,ZnCl\cdot OH$, micro-

scopic prisms, have been prepared; the *hydroxide* is not hygroscopic, and is comparatively stable, not being decomposed by boiling water.

<div align="right">C. S.</div>

Oxonium Compounds. GEORGE L. STADNIKOFF (*Ber.*, 1913, **46**, 2496—2503. Compare A., 1912, i, 109, 971).—In connexion with the conclusion drawn by the author from the occurrence of tetraphenylethane and αα-diphenylbutane after the action of water on the reaction product of diphenylmethyl butyl ether and magnesium propyl iodide, that the additive compound of the latter two substances is of the structure $\mathrm{CHPh_2}^{\mathrm{C_4H_9}}{>}\mathrm{O}{<}^{\mathrm{Pr}}_{\mathrm{MgI}}$, it may be objected that the formation of the tetraphenylethane and αα-diphenylbutane possibly preceded the addition of water.

To meet this objection, diphenylmethyl butyl ether has been allowed to react with various magnesium alkyl haloids in solution in ether (which does not prevent the formation of such additive compounds) for considerable periods. The procedure was to add the diphenylmethyl butyl ether to the cooled ethereal solution of the magnesium alkyl haloid and to find the quantities of any gaseous products evolved on boiling, and of the total organic products obtained on subsequently treating the cooled reaction product with water.

There are three main directions of decomposition of the ether additive compound which is believed to be the primary product on the addition of water : (1) the regeneration of diphenylmethyl butyl ether ; (2) the formation of tetraphenylethane, and (3) the production of a αα-diphenyl-substituted paraffin hydrocarbon.

With diphenylmethyl butyl ether and magnesium propyl iodide all the above reactions occur, although the relative amounts of the different products vary from those obtained earlier (A., 1912, i, 971) with the same Grignard reagent in the absence of ethyl ether. The results, however, confirm the author's views.

Diphenylmethyl butyl ether was allowed to form additive compounds also with magnesium ethyl iodide and magnesium methyl iodide ; the former gave similar results to the propyl compound ; the latter gave as hydrocarbon products only methane and tetraphenylethane.

Magnesium propyl iodide either in benzene or in ethereal solution when treated with diphenylmethyl *iso*amyl ether, and subsequently with water, gave propane and unaltered diphenylmethyl *iso*amyl ether.

In each case, except with the methyl Grignard reagent, a quantity of the corresponding ethylenic hydrocarbon was evolved during the heating after the addition of the "mixed" ether.

<div align="right">D. F. T.</div>

The Isomerism of Tri-α-naphthylcarbinol. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1913, **46**, 2554—2556).—The author is of opinion that of the so-called isomeric forms of tri-α-naphthylcarbinol described by Schmidlin and Bergmann (this vol., i, 46), the more stable is in reality merely the ether-free carbinol described earlier by himself (A., 1911, i, 969), and is not identical with the stable "isomeride" obtained by Schmidlin and Massini (A., 1909, i, 563), which he has

shown to be an oxidation product, namely, α-naphthyldi-αα-naphtha-fluoryl alcohol.   This view receives further confirmation from the fact that the free tri-α-naphthylcarbinol when dissolved in amyl acetate and treated with much ether is slowly deposited in needles or prisms of the easily oxidisable substance containing ether of crystallisation. The ether-free carbinol has a higher m. p., namely, 160—180° (decomp.), than that recorded hitherto.

There is consequently here no case of isomerism unless the compound containing ether of crystallisation is regarded as a distinct isomeride of the ether-free substance.   D. F. T.

Aromatic Selenium Compounds.   II.   RUDOLF LESSER and R. WEISS (*Ber.*, 1913, **46**, 2640—2658.   Compare A., 1912, i, 642). —An extended account of the results of attempts to prepare compounds containing a selenium atom in place of a sulphur atom, a preliminary note of which has previously appeared (*loc. cit.*).

Diphenyldiselinide-di-*o*-carboxylic acid, $Se_2(C_6H_4·CO_2H)_2$, is more conveniently prepared by the addition of a diazotised solution of anthranilic acid to a solution of potassium or sodium diselinide in an atmosphere of carbon dioxide.   After decomposition of the diazo-compound by heat, the acids are liberated by addition of mineral acid to the hot solution.   The crude diphenyldiselinide-di-*o*-carboxylic acid is freed from diphenylselinide-di-*o*-carboxylic acid by digestion with glacial acetic acid, which leaves the former undissolved.

o-*Methylselenolbenzoic acid*, $SeMe·C_6H_4·CO_2H$, long needles, m. p. 180—181°, is obtained in practically quantitative yield when an alkaline solution of sodium *o*-selenolbenzoate is shaken with methyl sulphate.   The corresponding *methyl* ester, m. p. 64—66°, is best obtained by the action of methyl iodide on the *silver* salt, and, in contrast with methyl *o*-methylthiolbenzoate, is odourless.   *o*-*Benzoyl-selenolbenzoic acid*, $SeBz·C_6H_4·CO_2H$, has m. p. 163—164°.

o-Selenonbenzoic acid, $SeO_3H·C_6H_4·CO_2H$, is a very strong acid, the salts of which are not decomposed by dilute nitric acid.   It has not been obtained in the crystalline state, but yields a *barium* salt, $C_7H_4O_5SeBa$, which separates from water in colourless, anhydrous needles.   An aqueous solution of the acid is transformed by hydro-chloric acid into *o*-seleninbenzoic acid, m. p. 228—229° (decomp.), which is also obtained by the oxidation of diphenyldiselenide-di-*o*-carboxylic acid by nitric acid, or a mixture of nitric and sulphuric acids.   When heated at 130—140° until constant in weight, it is transformed into the *anhydride*, $O(SeO·C_6H_4·CO_2H)_2$, without change in m. p.

When diphenyldiselenide-di-*o*-carboxylic acid is warmed with thionyl chloride and excess of the latter removed, a crystalline residue is obtained which can be separated by means of light petroleum into two portions.   The smaller of these, m. p. 173—174°, is the normal chloride, $C_{14}H_8O_2Cl_2Se_2$, whilst the larger, m. p. 65—66°, consists of a *compound* of this substance and hydrogen chloride, and has the composition $C_{14}H_{10}O_2Cl_4Se_2$.   When the latter is boiled with methyl alcohol, the *hydrochloride* of *methyldiphenyl-diselenide-di-o-dicarboxylate*, $C_{16}H_{16}O_4Cl_2Se_2$, yellow needles, m. p. 74—75°, is obtained, which, when treated with warm sodium hydroxide, is converted into the corresponding *ester*, m. p. 143—144°.   The *hydrochloride* of the *ethyl*

ester, m. p. 91—92°, is similarly formed and converted in the same manner into the *ethyl* ester, m. p. 129—130°. The normal esters can also be prepared by the action of the requisite alcohol on the normal chloride or on the free acid in the presence of hydrogen chloride.

Phosphorus pentachloride resembles thionyl chloride in its action on the free acid, yielding, however, a less pure product which contains a rather greater proportion of the normal chloride.

Pure diphenylselenide-di-*o*-carboxylic acid has m. p. 234—235° (instead of 228—229° as previously given). Thionyl chloride converts it into the corresponding normal *chloride*, lemon-yellow crystals, m. p. 107—108°, which gradually decomposes when preserved without, however, yielding a uniform product. Boiling methyl and ethyl alcohols transform the chloride into the *methyl* ester, m. p. 70—71°, and the *ethyl* ester, m. p. 64—65°, respectively. The *amide* forms colourless plates, m. p. 212—213°.

When warmed with concentrated sulphuric acid on the water-bath, diphenylselenide-di-*o*-carboxylic acid yields two products which can be separated by means of sodium hydroxide. The soluble portion consists of *selenoxanthone-o-carboxylic acid*, $C_6H_4\!<\!^{CO}_{Se}\!>\!C_6H_3\cdot CO_2H$, which sublimes from 250° in yellow needles and decomposes at 290—300°. In the dry state it is stable, but, when dissolved, readily eliminates carbon dioxide, for example, when a hot solution of its alkali salt is acidified. Attempts to transform it into the corresponding selenoxanthone by loss of carbon dioxide were, however, unsuccessful, benzophenone-selenone, $C_6H_4\!<\!^{CO}_{SeO_2}\!>\!C_6H_4$, being invariably produced. This substance also constitutes the portion obtained in the above action which is insoluble in alkali and is obtained as by-product of the action of thionyl chloride on diphenylselenide-di-*o*-carboxylic acid. It forms large, glassy prisms, m. p. 317—318° (decomp.), and sublimes partly undecomposed from about 260°. It thus differs remarkably from the benzophenoneselenone described by Doughty and Elder (this vol., i, 962) for which the m. p. 183° is given.

Acetic anhydride is without action on diphenylselenide-di-*o*-carboxylic acid, whilst potassium permanganate, in neutral or alkaline solution, converts it into the selenone.

o-Carboxyphenylselenolacetic acid is readily converted into its *methyl* ester, leaflets, m. p. 62—63°, by means of methyl alcohol and hydrogen chloride. The ethyl ester is oily.

When a diazotised solution of *m*-aminobenzoic acid is added to a solution of potassium hydrogen selenide or of potassium diselenide under the conditions described for anthranilic acid, *diphenylselenide-di-m-carboxylic acid* is produced, the diselenide acid being apparently not formed. It has m. p. 296—297°, and sublimes from about 260°. Concentrated sulphuric acid dissolves it with a yellow colour; fuming sulphuric acid with an intense bluish-green colour. Potassium permanganate oxidises it in the form of its salts to *diphenylselenon-di-m-carboxylic acid*, colourless prisms, which becomes yellow at about 255°, and has m. p. 262—263° (decomp.).

p-Aminobenzoic acid, when similarly treated, yields a difficultly separable mixture of the *p*-diselenide and selenide acids. *Diphenyl-*

*diselenide-di-*p-*carboxylic acid* is a pale yellow, crystalline powder, m. p. 314—315°. *Diphenylselenide-di-*p-*carboxylic acid*, two preparations of which had m. p. 312—313° and 315—316°, resembles the above acid so closely that it can only be distinguished from it by ultimate analysis.

Hydroxyselenonaphthen reacts with 5-bromoisatin in alcoholic solution in the presence of piperidine to form "2-*selenonaphthen*-[5-*bromo*-3-*indole*]-*indigo*" (3'-*bromoindoxyl*-2-*selenonaphthen*-3-*one*),

$$C_6H_4{<}^{CO}_{Se}{>}C{:}C{<}^{CO---}_{C_6H_3Br}{>}NH,$$
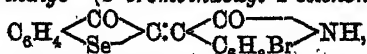
red, silky needles, which sublime at about 260°, have m. p. about 355°, and are soluble in fuming sulphuric acid, yielding a sulphonic acid which is soluble in water. Similarly, 3'-*methylindoxyl*-2-*seleno-naphthen*-3-*one* (red needles which sublime at about 250°, and have m. p. approximately 325—330°) is obtained from methylisatin, whilst by heating molecular quantities of isatin chloride and hydroxyseleno-naphthen in benzene solution, "2-*selenonaphthen*-2-*indole-indigo*" [2'-*indoxyl*-2-*selenonaphthen*-3-*one*], $C_6H_4{<}^{CO}_{NH}{>}C{:}C{<}^{CO}_{Se}{>}C_6H_4$, is formed. It consists of blackish-violet needles, which sublime undecomposed at approximately 250°, and have m. p. about 335°.

A series of condensation products of hydroxyselenonaphthen with aldehydes and fluorenone has been prepared by boiling molecular quantities of their components in methyl- or ethyl-alcoholic or glacial acetic acid solution in the presence of a few drops of concentrated hydrochloric acid. In general, the compounds are rapidly precipitated in good yield. They dissolve unchanged in concentrated sulphuric acid, but are converted by the fuming acid into sulphonic acids which dissolve in water. The following compounds have been prepared: Glyoxal yields the *substance*,

$$C_6H_4{<}^{CO}_{Se}{>}C{:}CH{\cdot}CH{:}C{<}^{CO}_{Se}{>}C_6H_4,$$
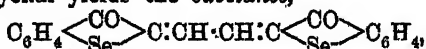
violet needles, m. p. 299—300°. Heptaldehyde and citral give oily products. *Furylidene*-2-*selenonaphthen*-3-*one*,

$$C_6H_4{<}^{CO}_{Se}{>}C{:}CH{\cdot}C_4H_3O,$$
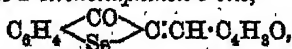
orange needles, m. p. 145—147°, p-*nitrobenzylidene*-2-*selenonaphthen*-3-*one*, reddish-golden needles or rods, m. p. 243—244°; 2:4-*dinitrobenzyli-dene*-2-*selenonaphthen*-3-*one*, which exists in two modifications, red or orange needles, both having m. p. 226—227° (decomp.); o-*hydroxy-benzylidene* - 2 - *selenonaphthen*-3-*one*, brownish-yellow rods, m. p. 206—207° (decomp.); o-*carboxybenzylidene* - 2 - *selenonaphthen*-3-*one*,

$$C_6H_4{<}^{CO}_{Se}{>}C{:}CH{\cdot}C_6H_4{\cdot}CO_2H,$$ yellow plates, m. p. 226—227°;

4-*hydroxynaphthylidene*-2-*selenonaphthen*-3 - *one*, red needles, m. p. 244—248°; 2-*methoxynaphthylidene* - 2 - *selenonaphthen*-3-*one*, yellow crystals, m. p. 127—128°; 2-hydroxynaphthaldehyde yields a *compound*, $C_{27}H_{16}O_2Se_2$, pale red crystals, m. p. 210—211° after previous darkening, which does not dissolve in sodium hydroxide, and appears to be derived from two molecules of hydroxyselenonaphthen and one of the aldehyde. Terephthalaldehyde yields the *substance*,

$$C_6H_4{<}^{CO}_{Se}{>}C{:}CH{\cdot}C_6H_4{\cdot}CH{:}C{<}^{CO}_{Se}{>}C_6H_4,$$ orange needles, which sub-

lime at about 296°, and have m. p. approximately 330°, whilst β-anthra-
quinonealdehyde gives the *compound*, $C_6H_4\underset{Se}{\overset{CO}{<}}\hspace{-2pt}>C{:}CH{\cdot}C_{14}H_7O_2$,
orange-red needles, subliming at about 270°, and having m. p.
348—349°. Prolonged warming with fluorenone in alcohlic solution
yields the *substance*, $C_6H_4\underset{Se}{\overset{CO}{<}}\hspace{-2pt}>C{:}C\underset{C_6H_4}{\overset{C_6H_4}{<}}$, deep red crystals, m. p.
169—171°.

p-Nitrobenzeneazo-3-hydroxyselenonaphthen,

$$C_6H_4\underset{Se}{\overset{C(OH)}{<}}\hspace{-2pt}>C{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2,$$
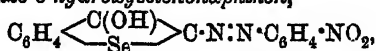
reddish-brown crystals, m. p. 239—241° (decomp.), is obtained by the
addition of p-nitrobenzene diazonium chloride to a solution of the
sodium salt of hydroxyselenonaphthen in the presence of sodium
acetate. H. W.

Diphenyleneacetic Acid [Fluorene - 9 - carboxylic Acid].
WILHELM WISLICENUS and ALEXANDER RUTHING (*Ber.*, 1913, **46**,
2770—2771).—An aqueous solution of fluorene-9-carboxylic acid and
sodium hydroxide (1 mol.) remains clear when kept in an atmosphere
of hydrogen. In the presence of oxygen, it rapidly becomes turbid
and deposits fluorenone; the yield of the latter is about 20% of the
theoretical, and is increased to about 50% when another mol. of sodium
hydroxide is present. At higher temperatures the decomposition
proceeds differently, an aqueous solution of sodium fluorene-9-
carboxylate at the b. p. yielding fluorene and sodium carbonate, most
readily when sodium hydroxide has been added. C. S.

Syntheses by means of Ethyl Diphenyleneacetate [Fluorene
9-carboxylate]. WILHELM WISLICENUS and WILLY MOCKER (*Ber.*,
1913, **46**, 2772—2793).—The *potassium* derivative of ethyl fluorene-
9-carboxylate is best obtained by adding rather more than the
theoretical quantity of alcohol to ethyl fluorene-9-carboxylate and
potassium (1 atom) in dry ether, a current of hydrogen being passed
through the apparatus. It is thus obtained as a yellow, microcrystal-
line powder containing EtOH, which decomposes rapidly in moist air,
and is converted in dry air into the additive *compound*,

$$\underset{C_6H_4}{\overset{C_6H_4}{<}}\hspace{-2pt}>C(OK){\cdot}CO_2Et,EtOH,$$
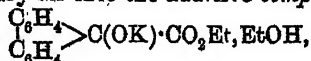
from which ethyl 9-hydroxyfluorene-9-carboxylate, m. p. 93°, is obtained
by the action of sulphuric acid. The *sodium* derivative,

$$C_{16}H_{13}O_3Na,EtOH,$$
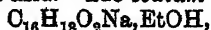
of ethyl fluorene-9-carboxylate is prepared in a similar manner and
reacts in the same manner with atmospheric oxygen. In consequence
of the easy oxidisability of the alkali derivatives of ethyl fluorene-
9-carboxylate, syntheses with these reagents must be effected in an
atmosphere of hydrogen, otherwise 9-hydroxyfluorene-9-carboxylic acid
is the final product.

The following syntheses have been performed. By treatment
with the calculated amount of iodine, a solution of the alkali
derivative, prepared as above, readily yields ethyl bisdiphenylene-
succinate [9 : 9'-difluorene-9 : 9'-dicarboxylate] (Staudinger, A.,

1906, i, 824), which cannot be hydrolysed to the corresponding acid. The solution of the potassium derivative and methyl iodide gives a nearly quantitative yield of *ethyl α-diphenylene-propionate* [9-*methylfluorene*-9-*carboxylate*], $\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}$>CMe·CO$_2$Et, b. p. 188—190°/14 mm., m. p. 33°, which, however, is not obtained quite pure by this method. 9-*Methylfluorene*-9-*carboxylic acid* yields 9-methyl-fluorene at 250°; the latter has b. p. 154—156°/15 mm. and m. p. 45°. *α-Diphenylenebutyric* [9-*ethylfluorene*-9-*carboxylic*] *acid*,

$$\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}>CEt·CO_2H,$$
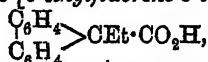
obtained in a similar manner by means of ethyl iodide, forms an *ethyl* ester, b. p. 200—205°/14—15 mm., and decomposes at 230—240° into carbon dioxide and 9-ethylfluorene. The latter is a liquid, b. p. 169—171°/14 mm., not a solid as stated by Wislicenus and Densch, and does not react with potassium even at 250°. 9-*Allylfluorene*-9-*carboxylic acid*, $\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}$>C(CO$_2$H)·CH$_2$·CH:CH, colourless prisms containing $\frac{1}{2}$C$_6$H$_6$ (*ethyl* ester, b. p. 200—203°/14 mm.), yields 9-*allyl-fluorene*, b. p. 174—176°/15 mm., at 240—250°. 9-*Benzylfluorene*-9-*carboxylic acid*, $\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}$>C(CO$_2$H)·CH$_2$Ph, m. p. 201—202°, colourless leaflets (*ethyl* ester, m. p. 90—91°), yields 9-benzylfluorene at 240—250°; the latter is also produced by boiling the ester with alcoholic potassium hydroxide.

Ethyl αα-bisdiphenyleneadipate [9 : 9'-*ethylenedifluorene*-9 : 9'-*dicarboxy-late*], $\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}$>C$<$$\begin{smallmatrix} CH_2 \\ CO_2Et \end{smallmatrix}$——$\begin{smallmatrix} CH_2 \\ CO_2Et \end{smallmatrix}$>C$<$$\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}$, m. p. 179—180°, colourless needles, prepared by the aid of ethylene dibromide, yields, by hydrolysis with alcoholic sodium hydroxide at the ordinary temperature and subsequent acidification, 9 : 9'-*ethylenedifluorene*-9 : 9'-*dicarboxylic acid*, m. p. about 260° (decomp.), *αδ-bisdiphenylenebutane* [9 : 9'-*ethylenedifluorene*], C$_2$H$_4$(C$_{13}$H$_9$)$_2$, colourless needles, being produced when the hydrolysis is effected on the water-bath.

Iodobenzene does not react with the solution of the potassium derivative of ethyl fluorene-9-carboxylate even at 150—180°. 1-Bromo-2 : 4-dinitrobenzene, however, yields ethyl 9-*op-dinitrophenylfluorene-carboxylate*, C$_{13}$H$_9$(CO$_2$Et)·C$_6$H$_3$(NO$_2$)$_2$, m. p. 130—131°, faintly yellow crystals, which cannot be hydrolysed to the corresponding acid. In a similar manner, ethyl chloroacetate yields *ethyl diphenylene-succinate* [9-*carboxyfluorene*-9-*acetate*],
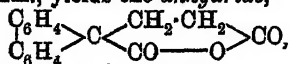
$$CO_2Et·C_{13}H_8·CH_2·CO_2Et,$$
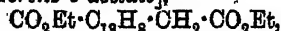
m. p. 73—75°, colourless crystals; by hydrolysis at the ordinary temperature, the ester yields the corresponding *acid*, C$_{16}$H$_{12}$O$_4$, m. p. 195—196° (decomp.), which is converted at its m. p. into its *anhydride*,

$$\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix}>C<\begin{smallmatrix} CO——O \\ CH_2·CO \end{smallmatrix}, \text{ m. p. 158—159°, b. p. about 255°/16 mm.}$$
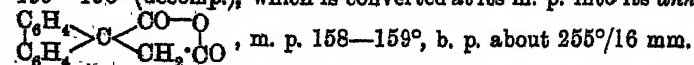
Ethyl β-iodopropionate reacts with the solution of the sodium or potassium derivative of ethyl fluorene-9-carboxylate to form, after hydrolysis of the impure ester, *α-diphenyleneglutaric* [9-*carboxyfluorene-*

9-*propionic*] *acid*, $CO_2H \cdot C_{13}H_8 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, m. p. 195—196°, colourless prisms or needles. The acid forms an *ethyl* ester, $C_{21}H_{22}O_4$, b. p. 235—240°/14 mm., yields the *anhydride*,
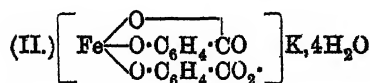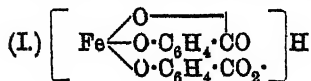
$$\begin{array}{c} C_6H_4 \\ C_6H_4 \end{array} > C < \begin{array}{c} CH_2 \cdot CH_2 \\ CO \quad\quad O \end{array} > CO,$$

m. p. 175—176°, colourless prisms, by boiling with acetyl chloride, and is converted into γ-*diphenylenebutyric* [*fluorene-9-propionic*] *acid*, $C_{16}H_{14}O_2$, m p. 148—149° (*ethyl* ester, b. p. 224—226°/17 mm.), by heating at about 260°.

Ethyl β-*benzoyl-α-diphenylenepropionate* [9-*phenacylfluorene-9-carboxylate*], $CO_2Et \cdot C_{13}H_9 \cdot CH_2 \cdot COPh$, m. p. 123—124°, obtained by means of ω-bromoacetophenone at about 80°, is converted by the action of aqueous alcoholic sodium hydroxide into *phenyl* β-*diphenylene-ethyl ketone* [9-*phenacylfluorene*], $C_{12}H_8 \cdot CH \cdot CH_2 \cdot COPh$, m. p. 96—97°, colourless needles. C. S.

Solubility of Salicylic Acid and of Some Other Substances. EGLIE SAVARRO (*Atti R. Accad. Sci. Torino*, 1913, **48**, 948—959).— Tables are given showing the solubility of salicylic acid at various temperatures, the figures obtained by previous observers being discordant. Some experiments have also been made on isomeric substances (compare Carnelley and Thompson, T., 1888, **53**, 782). The solubilities of the three hydroxybenzoic acids in water at 15° and at 50° increase in the order: ortho, para, meta, whilst those in methyl alcohol follow the order of the melting points: ortho, meta, para. According to the law of Carnelley and Thompson the order of solubilities should be para, meta, ortho. The solubilities in methyl alcohol of four pairs of isomeric pyridine derivatives prepared by Guareschi (*Atti R. Accad. Sci. Torino*, 1900–01, **50**) have also been determined; here the law already mentioned is followed with some exceptions. R. V. S.

Iron Compounds of Phenols. V. Iron Compounds of Salicylic Acid. RUDOLF F. WEINLAND and ALFRED HERZ (*Annalen*, 1913, **400**, 219—268. Compare this vol., i, 458).—The reaction between alkali salicylates and ferric salts in aqueous or alcoholic solution gives rise to very complex iron derivatives of salicylic acid. Their formation is due to the fact that salicylic acid forms, by virtue of its phenolic hydroxyl group, di- and tri-salicylatoferric acids analogous to the catecholferric acids (A., 1912, i, 445), and, by virtue of its carboxyl group, a hexasalicylatotriferric hydroxide analogous to hexabenzoatotriferric hydroxide (A., 1912, i, 854); this complex base can then react with the complex acids to form still more complex salts. In the preparation of the following substances, the concentrations of the reacting solutions and the order of their addition are matters of great importance. All quantities mentioned below are in atomic or molecular proportions.

(I.) $\left[Fe \left< \begin{array}{c} O \quad\quad\quad \\ O \cdot C_6H_4 \cdot CO \\ O \cdot C_6H_4 \cdot CO_2 \cdot \end{array} \right] H \right.$

(II.) $\left[Fe \left< \begin{array}{c} O \quad\quad\quad \\ O \cdot C_6H_4 \cdot CO \\ O \cdot C_6H_4 \cdot CO_2 \cdot \end{array} \right] K,4H_2O \right.$

Salts of Disalicylatoferric Acid (I). —*Potassium disalicylatoferrate* (II), dark copper-red powder, is obtained by adding aqueous ferric chloride to aqueous salicylic acid and potassium hydroxide ($Fe : C_7H_6O_3 : KOH = 1 : 4 : 7$).

Rubidium disalicylatoferrate, dark copper-red powder, is obtained in a similar manner ($Fe : C_7H_6O_3 : RbOH = 1 : 3 : 6$). These two salts form blood-red aqueous solutions, which change to violet by the addition of hydrochloric acid or of ferric chloride, and yield hexasalicylatotriferric monosalicylate (see below) by treatment with dilute acetic acid.
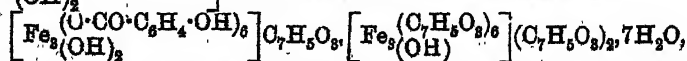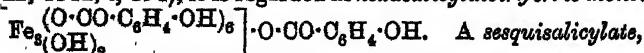
Salts of Trisalicylatoferric Acid, $\left[Fe_{(C_6H_4\cdot CO_2)_3}^{\quad O}\right]H_3$.—The gradual addition of very dilute aqueous ferric chloride to concentrated aqueous sodium salicylate produces successively a reddish-yellow, blood-red, and finally violet solution. The blood-red solution contains sodium disalicylatoferrate, and the violet solution a ferric salt of this acid (see below). The reddish-yellow solution contains *sodium trisalicylatoferrate*, which, however, cannot be isolated from aqueous solution. *Potassium trisalicylatoferrate*, $[Fe(C_7H_4O_3)_3]K_3,1\frac{1}{2}H_2O$, brick-red, crystalline powder, is obtained from ferric acetate [of the composition $Fe_6(OAc)_{15}(OH)_3,3H_2O$], potassium salicylate, and potassium hydroxide in 96% alcohol ($Fe : C_7H_6O_3 : KOH = 1 : 4 : 7$). The *rubidium* salt, orange-red, crystalline powder containing $2H_2O$, is obtained in a similar manner. These salts are easily soluble in water, but the solutions rapidly decompose; however, if the alkali salicylate is also present, the solutions can be boiled without decomposition.

The free di- and tri-salicylatoferric acids have not been isolated. The union of the iron with the phenolic oxygen of the acid complex is proved by the fact that ferric acetate, methyl salicylate, and potassium hydroxide ($Fe : C_8H_8O_3 : KOH = 1 : 15 : 3$) in alcoholic solution yield *potassium tetramethylsalicylatoferrate*, $[Fe(C_7H_4O_3Me)_4]K$, reddish-brown, crystalline powder.
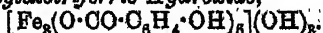
Salts of Hexasalicylatotriferric Hydroxide,
$$[Fe_3(O\cdot CO\cdot C_6H_4\cdot OH)_6](OH)_3.$$
—The reddish-yellow, blood-red, and violet solutions obtained, according to the quantities of the reagents used, by the addition of aqueous ferric chloride (at least 1 mol.) to a not too dilute aqueous solution of sodium salicylate (4 mols.) soon yield reddish-brown precipitates. By keeping in the mother liquor, these precipitates soon change to a black, crystalline substance (compare Hopfgartner, A., 1908, i, 891). The reddish-brown substance can be isolated unchanged if ether is added to either solution before the solutions of ferric chloride and sodium salicylate ($Fe : Na = 1 : 3$) are mixed; by shaking, the salicylic acid liberated in the reaction is removed from the aqueous phase, and the precipitate then remains unchanged. The same substance is also obtained unchanged when hot solutions of ferric chloride and sodium salicylate are mixed. It has been isolated as a brown powder containing $3H_2O$, and also as a reddish-brown, crystalline powder containing $2EtOH,2H_2O$. Since the ratio of iron to salicylic acid is 3 : 7 and the substance behaves like hexabenzoatotriferric monobenzoate A., 1912, i, 854), it is regarded as *hexasalicylatotriferric monosalicylate,*
$$Fe_3^{(O\cdot CO\cdot C_6H_4\cdot OH)_6}_{(OH)_2}\Big]\cdot O\cdot CO\cdot C_6H_4\cdot OH. \quad \text{A } sesquisalicylate,$$
$$\left[Fe_3^{(O\cdot CO\cdot C_6H_4\cdot OH)_6}_{(OH)_2}\right]C_7H_5O_3,\left[Fe_3^{(C_7H_5O_3)_6}_{(OH)}\right](C_7H_5O_3)_2,7H_2O,$$
of the base is obtained as a red, crystalline powder (which rapidly becomes almost black) by treating the preceding substance with a

warm saturated solution of salicylic acid in acetone; chloroform or ethyl alcohol may also be used as the solvent, in the latter case the sesquisalicylate being obtained as a reddish-brown, crystalline powder containing $3EtOH$ and $9H_2O$.

The ferrisalicylic acid described by Hantzsch and Desch (A., 1902, i, 708) contains acetic acid and is in reality *hexasalicylatotriferric diacetate*, $\left[Fe_3{(O \cdot CO \cdot C_6H_4 \cdot OH)_6 \atop (OH)}\right](OAc)_2, 3Et_2O$, garnet-red prisms (from ether); by heating at $100°$, it changes to the *monoacetate*, $\left[Fe_3{(O \cdot CO \cdot C_6H_4 \cdot OH)_6 \atop (OH)_2}\right] \cdot OAc$. Other salts of hexasalicylatotriferric hydroxide have been obtained by the reaction between lithium salicylate and ferric chloride, bromide, or nitrate in alcoholic solution; in some of these reactions a little water must be added. None of these salts contains iron and salicylic acid in a ratio less than $3:6$; therefore, they are regarded as complex derivatives of the hexasalicylatotriferric base. Thus lithium salicylate and ferric chloride yield, according to the proportions of the reagents, a *chloride salicylate*, $\left[Fe_3{(O \cdot CO \cdot C_6H_4 \cdot OH)_6 \atop (OH)}\right]{O \cdot CO \cdot C_6H_4 \cdot OH \atop Cl}, 4\frac{1}{2}H_2O$, red, crystalline powder, or a double *salt* of the chloride and the chloride salicylate,

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right]Cl, \left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop Cl}, H_2O,$$

red, amorphous powder (which becomes crystalline after two days), or a double *salt* of the salicylate and the chloride salicylate,

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right]C_7H_5O_3, 2\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop Cl}, 11H_2O,$$

brownish-red, crystalline powder. Ferric bromide ($Fe_2Br_6, 6H_2O$, see below) forms a double *salt*,

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right]C_7H_5O_3, 2\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop Br}, 11H_2O,$$

carmine, crystalline powder, and ferric nitrate yields a double *salt*,

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right]C_7H_5O_3, \left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop NO_3}, 2H_2O,$$

reddish-yellow, crystalline powder.

The great similarity between the salts of hexabenzoatotriferric hydroxide and hexasalicylatotriferric hydroxide indicates that in the latter the iron is attached to the carboxyl group of the salicylic acid, as represented in the preceding formulæ. This is also proved by the fact that salts of a similar base, *hexa-o-methoxybenzoatotriferric hydroxide*, can be obtained from o-methoxybenzoic acid. Thus by treating aqueous ferric chloride with aqueous sodium o-methoxybenzoate ($Fe:Na = 1:3$) or with warm aqueous o-methoxybenzoic acid ($Fe:acid = 1:3$), *hexa-o-methoxybenzoatotriferric mono-o-methoxybenzoate*,

$$\left[Fe_3{(O \cdot CO \cdot C_6H_4 \cdot OMe)_6 \atop (OH)_2}\right] \cdot O \cdot CO \cdot C_6H_4 \cdot OMe, 7\frac{1}{2}H_2O,$$

is obtained as a yellow, crystalline substance; its alcoholic solution reacts with 20% perchloric acid to form the *perchlorate*,

$$\left[Fe_3{(O \cdot CO \cdot C_6H_4 \cdot OMe)_6 \atop (OH)_2}\right]ClO_4, H_2O,$$

orange-yellow leaflets.

In a similar manner, by treating aqueous ferric chloride with sodium *m*- or *p*-hydroxybenzoate (Fe : Na = 1 : 3), *hexa*-m-*hydroxy-benzoatotriferric mono*-m-*hydroxybenzoate*

$$\left[Fe_3 \frac{(O \cdot CO \cdot C_6H_4 \cdot OH)_6}{(OH)_2} \right] \cdot O \cdot CO \cdot C_6H_4 \cdot OH, 5H_2O,$$
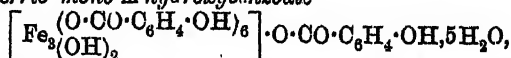
dark brown powder, and the corresponding para-*isomeride*, brown, prismatic crystals, are obtained. The latter reacts with 5% aqueous ferric chloride in excess to form *p*-hydroxybenzoic acid and a very soluble *substance*, garnet-red prisms, which contains Fe : Cl : $C_7H_5O_3$ = 1 : 1 : 1, and is regarded as having the constitution

$$\left[Fe_3(O \cdot CO \cdot C_6H_4 \cdot OH)_6 \right]\left[Fe \frac{Cl_2}{(OH)_2} \right]_3, 10H_2O.$$
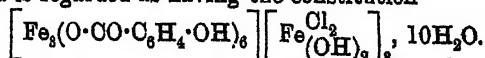
Hexa-p-*hydroxybenzoatotriferric chloride* p-*hydroxybenzoate*,

$$\left[Fe_3 \frac{(O \cdot CO \cdot C_6H_4 \cdot OH)_6}{(OH)} \right] \frac{Cl}{O \cdot CO \cdot C_6H_4 \cdot OH}, 1\tfrac{1}{2}H_2O,$$
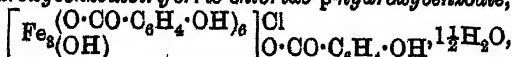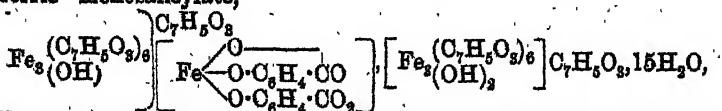
brown, crystalline powder, is obtained by the reaction of ferric chloride and lithium *p*-hydroxybenzoate (Fe : Li = 1 : 1·5) in alcohol containing a little water.
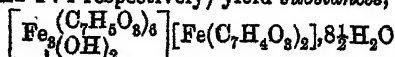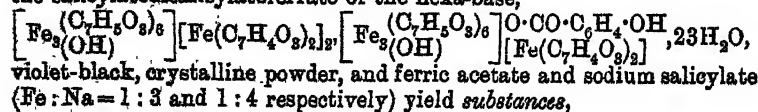
Compounds of Hexasalicylatotriferric Hydroxide and the Salicylato-ferric Acids or a Salicylatoferrous Acid.—The reddish-brown precipitate obtained from aqueous ferric chloride and sodium salicylate (Fe : Na = 1 : 3) changes by keeping in the mother liquor for about a day to a black, crystalline *substance* (the streak is violet), which contains Fe : $C_7H_5O_3$ = 4 : 9, not 1 : 2 (compare Hopfgartner, *loc. cit.*), and is regarded as *hexasalicyl-atotriferric sali-cylate disali-cylatoferrate* (annexed formula).

$$\left[Fe_3 \frac{(O \cdot CO \cdot C_6H_4 \cdot OH)_6}{(OH)} \right]\left[Fe \begin{matrix} O \cdot CO \cdot C_6H_4 \cdot OH \\ O \\ O \cdot C_6H_4 \cdot CO \\ O \cdot C_6H_4 \cdot CO_2 \end{matrix} \right], 8\tfrac{1}{2}H_2O.$$
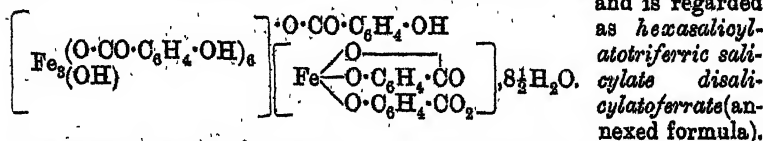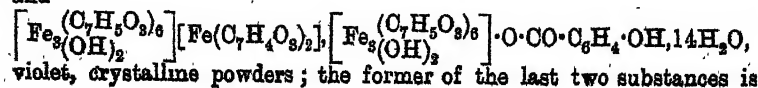
In a similar manner, by keeping the initial reddish-brown precipitates in the mother liquors, ferric nitrate and sodium salicylate (Fe : Na = 1 : 3) yield a double *compound* of the preceding salt and hexasalicylato-triferric monosalicylate,

$$\left[Fe_3 \frac{(C_7H_5O_3)_6}{(OH)} \right]\left[Fe \begin{matrix} C_7H_5O_3 \\ O \\ O \cdot C_6H_4 \cdot CO \\ O \cdot C_6H_4 \cdot CO_2 \end{matrix} \right], \left[Fe_3 \frac{(C_7H_5O_3)_6}{(OH)_2} \right] C_7H_5O_3, 15H_2O,$$

black, crystalline powder, ferric sulphate and sodium salicylate (Fe : Na = 1 : 1·5) yield a double *salt* of the bisdisalicylatoferrate and the salicylatedisalicylatoferrate of the hexa-base,

$$\left[Fe_3 \frac{(C_7H_5O_3)_6}{(OH)} \right][Fe(C_7H_4O_3)_2]_2, \left[Fe_3 \frac{(C_7H_5O_3)_6}{(OH)} \right]\frac{O \cdot CO \cdot C_6H_4 \cdot OH}{[Fe(C_7H_4O_3)_2]}, 23H_2O,$$

violet-black, crystalline powder, and ferric acetate and sodium salicylate (Fe : Na = 1 : 3 and 1 : 4 respectively) yield *substances*,

$$\left[Fe_3 \frac{(C_7H_5O_3)_6}{(OH)_2} \right][Fe(C_7H_4O_3)_2], 8\tfrac{1}{2}H_2O$$

and

$$\left[Fe_3 \frac{(C_7H_5O_3)_6}{(OH)_2} \right][Fe(C_7H_4O_3)_2], \left[Fe_3 \frac{(C_7H_5O_3)_6}{(OH)_2} \right] \cdot O \cdot CO \cdot C_6H_4 \cdot OH, 14H_2O,$$

violet, crystalline powders ; the former of the last two substances is

also obtained from the reddish-brown precipitate resulting from the addition of dilute acetic acid to cold saturated aqueous potassium disalicylatoferrate (see above).
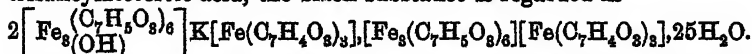
The compositions of the preceding complex salts are deduced from the ratio of the iron to the salicylic acid in them, and are most simply explained by assuming that the violet and black substances are salts of hexasalicylatotriferric hydroxide and salicylic or di- or tri-salicylato-ferric acid. Thus the violet substance, two methods of preparing which are mentioned above, contains iron and salicylic acid in the ratio $4:8$ $(1:2)$, and is therefore hexasalicylatotriferric disalicylato-ferrate. Again, the reddish-yellow, aqueous solution obtained from ferric chloride, salicylic acid, and potassium hydroxide

$$(Fe:C_7H_6O_3:KOH=1:3:5)$$
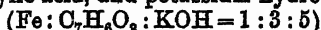
deposits a reddish-brown precipitate which changes to a *substance*, black, crystalline powder (violet streak), which contains

$$Fe:C_7H_6O_3:K=12:27:2\ ;$$
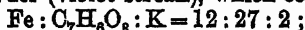
since reddish-yellow solutions are indicative of the alkali salt of trisalicylatoferric acid, the black substance is regarded as

$$2\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]K[Fe(C_7H_4O_3)_3],[Fe_3(C_7H_5O_3)_6][Fe(C_7H_4O_3)_3],25H_2O.$$

The preceding complex salts of the hexa-base differ from the simpler salts of the base mentioned under the third section in their black or violet colour, and in their insolubility in alcohol, acetone, and ether. Hexasalicylatotriferric monosalicylate changes to the violet and black salts of the hexa-base in the presence of water, and, conversely, the violet and black salts are converted into hexasalicylatotriferric mono-salicylate by alcoholic salicylic acid; hence the changes hexa-base $\underset{\substack{\text{alcohol}\\ \text{and } C_7H_6O_3}}{\overset{H_2O}{\rightleftarrows}}$ disalicylatoferric acid are partly the cause of the large number of the iron compounds of salicylic acid.

The violet and black salts are very sparingly soluble in water, forming faintly violet solutions. Possibly the intensely violet colora-tion developed in the usual ferric chloride test for salicylic acid is due to the formation of a salt of disalicylatoferric acid containing a complex iron cation such as $[Fe(H_2O)_6]$ (salts of disalicylatoferric acid con-taining a simple cation such as potassium or sodium are red); such a salt would be more soluble than the violet or black salts described above, and would, therefore, produce a more intensely violet colora-tion. The authors have been unable to isolate such a salt; they have prepared, however, a *salt* of the hexasalicylatotriferric and hexa-acetotriferric hydroxides with disalicylatoferric acid, $\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right][Fe(C_7H_4O_3)_2],[Fe_3(OAc)_6](OH)_3,4H_2O$, which is much more soluble in water than the violet and black salts, forming a reddish-violet solution changing to violet by the addition of hydrochloric acid, owing to the decomposition of the hexa-aceto-base.

Intensely violet solutions are obtained from aqueous sodium salicylate and an excess of ferric chloride, from aqueous salicylic acid and ferric chloride, and from all the salts of hexasalicylatotriferric hydroxide by warming them with very dilute hydrochloric acid; in all

these cases, disalicylatoferric acid and (complex) iron cations, that is, the two components necessary for the production of the intensely violet ferric disalicylatoferrate, are formed. Conversely, the addition of soium sal icylate or of sodium carbonate to solutions of salts of hexasalicylatotriferric hydroxide produces, according to the relative quantities of the reagents, red solutions of sodium disalicylatoferrate or reddish-yellow solutions of sodium trisalicylatoferrate. Similarly, the addition of aqueous calcium hydrogen carbonate to the violet solution produces a red solution of calcium disalicylatoferrate.

The residue obtained by the evaporation of aqueous ferric bromide has the composition $Fe_2Br_8,6H_2O$, and contains ferrous iron. In alcoholic solution it reacts with lithium salicylate ($Fe:Li = 1:3$) to form a *substance*, olive-brown crystals, which contains

$$Fe^{III}:Fe^{II}:C_7H_6O_3 = 3:1:9,$$

and is therefore regarded as *hexasalicylatotriferric salicylate disalicylatoferrite*, $\left[Fe_3{}^{III}(C_7H_5O_3)_6 \right]\begin{matrix} O\cdot CO\cdot C_6H_4\cdot OH \\ [Fe^{II}(C_7H_4O_3)_2] \end{matrix},6H_2O$. The same substance is obtained from lithium salicylate and alcoholic ferric chloride which has been partly reduced by the addition of iron. An alcoholic solution of $Fe_2Br_8,6H_2O$, which has been still further reduced by iron, reacts with lithium salicylate ($Fe:Li = 1:3$) to form *hexasalicylatotriferric hydrogen trisdisalicylatoferrite*,

$$[Fe_3{}^{III}(C_7H_5O_3)_6]H_3[Fe^{II}(C_7H_4O_3)_2]_3,5\tfrac{1}{2}H_2O,$$
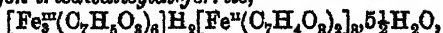
blackish-brown, crystalline powder.   C. S.

Methylcarbonato-derivatives of Hydroxy-acids. EMIL FISCHER and HERMANN O. L. FISCHER (*Ber.*, 1913, 46, 2659—2664).—Hydroxy-acids either do not react with methyl chloroformate in aqueous alkaline solution or give very poor yields of methylcarbonato-derivatives. The latter, however, are readily obtained by the combined action of methyl chloroformate and tertiary bases on hydroxy-acids dissolved in anhydrous solvents (compare Fischer, A., 1909, i, 161).

r-*Methylcarbonatomandelic acid*, $CO_2Me\cdot O\cdot CHPh\cdot CO_2H$, is obtained by the addition of methyl chloroformate to a well cooled solution of had r-mandelic acid in a mixture of chloroform and dimethylaniline. It m. p. 118—119° (corr.), after slight softening, and begins to decompose at about 140°. Alkalis readily transform it into r-mandelic acid, for which the authors give m. p. 120·5° (corr.) after previous softening, instead of 118° as recorded in the text books. r-*Methylcarbonatomandelyl chloride*, colourless prisms, m. p. 39—40°, is obtained by the action of phosphorus pentachloride at the ordinary temperature on a solution of the acid in chloroform, and is converted by cold methyl alcohol into *methyl r-methylcarbonatomandelate*, $CO_2Me\cdot O\cdot CHPh\cdot CO_2Me$, prisms, m. p. 51—52°. This ester is rapidly saponified by sodium hydroxide when dissolved in aqueous acetone; when two and a-half molecules of alkali are used, mandelic acid is formed, but when only one molecule is employed, methylcarbonatomandelic acid is the main product.

When mixed with an excess of aniline in ethereal solution, methyl-carbonatomandelyl chloride yields a *compound*, $C_{16}H_{15}O_4N$, needles,

m. p. about 142° (corr. decomp.), which is converted by prolonged contact with 2N-sodium hydroxide (2 mols.) into an acid which melts with decomposition, and has not been completely investigated. In any case, normal formation of the anilide of mandelic acid does not occur, and the authors therefore do not assign a definite structure to the aniline compound.

Glycollic acid reacts with methyl chlorocarbonate in a manner similar to mandelic acid, but yielding a product which is difficult to purify.

The authors have also prepared a compound from r-mandelic acid and acetylcarbimide in the expectation that the latter group would be readily eliminated, and that the product could thus be used in place of the methylcarbonato-derivatives. This is, however, not the case, since the re-conversion into mandelic acid does not occur with sufficient ease.

r-*Acetylaminocarboylmandelic acid*, $NHAc\cdot CO\cdot O\cdot CHPh\cdot CO_2H$, colourless needles, m. p. about 168—169° (decomp.), is obtained by the gradual addition of acetylcarbimide to a solution of well dried r-mandelic acid in anhydrous ether. It is converted by 2N-sodium hydroxide at the ordinary temperature into the *urethane* of *mandelic acid*, $NH_2\cdot CO\cdot O\cdot CHPh\cdot CO_2H$, m. p. 172—173° (corr. decomp.), when quickly heated.   H. W.

Hydrogenation of Santonin. HEINRICH WIENHAUS (*Ber.*, 1913, **46**, 2836—2839).—Polemical. The author assumes the presence of two conjugated double bonds in santonin based on the fact that at the ordinary temperature and without increased pressure in neutral solution it takes up four atoms of hydrogen (compare Weinhaus and Oettingen, this vol., i, 474; Wedekind and Beniers, this vol., i, 476; Angeli, this vol., i, 864).

Chromosantonin gives the same products on hydrogenation in presence of colloidal palladium chloride as santonin.   E. F. A.

Hydrogenation of Santonic Acid. Dihydrosantonin. GUIDO CUSMANO (*Annalen*, 1913, **400**, 332—337).—Results already recorded (this vol., i, 864).   C. S.

Action of Sodium Hypochlorite on Amides of Unsaturated Acids. RUDOLF A. WEERMAN (*Annalen*, 1913, **401**, 1—20. Compare A., 1906, i, 665; 1907, i, 132; 1908, i, 22; 1909, i, 589).—Freundler, van Linge, Jeffreys, and Baucke have attempted unsuccessfully to apply Hofmann's reaction to the production of amines from unsaturated acid amides.

Finely-powdered cinnamamide, by shaking with amyl alcohol and aqueous sodium hypochlorite, is converted into the *chloroamide*, $CHPh{:}CH\cdot CO\cdot NHCl$, m. p. 125° (decomp.), white plates, which yields *barium styrylcarbamate*, $Ba(C_9H_8O_2N)_2$, by treatment with aqueous barium hydroxide. The salt yields only a trace of phenylacetaldehyde by treatment with even the weakest acids; however, by decomposition with sodium hydrogen sulphite or hydroxylamine hydrochloride, the aldehyde is obtained in the form of its sodium hydrogen sulphite compound or oxime respectively.

The following substances are obtained by reactions similar to the preceding.

o-*Nitrocinnamchloroamide*, m. p. 142° (decomp.), colourless needles, is converted into *barium o-nitrostyrylcarbamate* by 0·3*N*-barium hydroxide on the water-bath; the latter yields o-*nitrophenylacetaldoxime*, m. p. 110°, colourless needles, with aqueous hydroxylamine hydrochloride.

m-*Nitrocinnamide*, m. p. 195—196°, prepared from the acid chloride and gaseous ammonia in benzene, is converted into *methyl* m-*nitrostyrylcarbamate*, m. p. 140°, yellow needles, from which m-*nitrophenylacetaldehyde*, $C_8H_7O_3N,H_2O$, m. p. 78—79°, can be prepared. m-*Nitrocinnamchloroamide*, m. p. 178° (decomp.), is converted as above into *barium* m-*nitrostyrylcarbamate*, yellow leaflets, from which m-*nitrophenylacetaldoxime*, m. p. 105—106°, colourless leaflets, can be obtained.

p-Nitrocinnamamide, m. p. 217° (not 155—160°, as stated by Chiozza in 1853), is converted by methyl alcohol and aqueous sodium hypochlorite into *methyl* p-*nitrostyrylcarbamate*, m. p. 188°, yellow needles, from which *p*-nitrophenylacetaldehyde, m. p. 85°, can be prepared. p-*Nitrocinnamchloroamide*, m. p. 169° (decomp.), colourless needles, is converted into *barium* p-*nitrostyrylcarbamate*, yellow needles, from which p-*nitrophenylacetaldoxime*, m. p. 155°, can be prepared.   C. S.

Camphenecarboxylamide and Hydrocamphenecarboxyl-amide. JOSEF HOUBEN and ERNST WILLFROTH (*Ber.*, 1913, **46**, 2530—2537).—The authors have recently shown (this vol., i, 970) that the action of methyl-alcoholic potash on methyl chloro*allo*camphanecarboxylate yields two isomeric unsaturated acids, the occurrence of which may be attributed to the unsymmetrical nature of chloro*allo*camphanecarboxylic acid or to the disturbing effect of the alkali on the single course of the reaction. The latter view receives support from the fact that chloro*allo*camphanecarboxylamide passes into a crystalline unsaturated amide, m. p. 210°, when merely boiled with water (*loc. cit.*), and the product appears to be free from any isomeride. Reduction of the unsaturated amide in acetic acid by platinum black and hydrogen causes a quantitative conversion into a saturated amide, *hydrocamphenecarboxylamide*, leaflets, m. p. 189°, which is quite distinct from *allo*camphanecarboxylamide. If the difference is not due to stereoisomerism, the above elimination of hydrogen chloride must therefore be accompanied by a change from the bornylene to the camphene group.

The mixture of unsaturated esters from methyl chloro*allo*camphanecarboxylate was then converted into the corresponding mixture of acids and treated with thionyl chloride; the resulting acid chlorides, when submitted together in ethereal solution to the action of ammonia, yielded two isomeric unsaturated amides, m. p. 209° and 98° respectively. The former, which preponderated, was identical with the amide (above) obtained by the action of water on the chlorine-substituted amide, and must be related to the camphenecarboxylic acid of m. p. 105°, whilst the latter amide, m. p. 98°, must be related to the second camphenecarboxylic acid.

The action of sodium nitrite and hydrochloric acid on the saturated amide, m. p. 189° (see above), gave a saturated acid, *hydrocamphene-carboxylic acid*, hexagonal leaflets, m. p. 126°, which is also obtainable by hydrolysis with hot concentrated hydrochloric acid.   D. F. T.

Preparation of Purpurin-3-carboxylic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 260765.   Compare Perkin and Cope, T., 1894, **65**, 848).—Purpurin-3-carboxylic acid, a red powder, m. p. 222—224° (with loss of carbon dioxide), is obtained when 1 : 2-dihydroxyanthraquinone-3-carboxylic acid dissolved in 20 parts of concentrated sulphuric acid is slowly treated at 15—20° with manganese dioxide (0·3—0·4 part); it is identical with the "ψ-purpurin" (purpurincarboxylic acid) present in madder.   F. M. G. M.

Preparation of 1:4-Diaminoanthraquinone-2-carboxylic Acid and of 1 : 4-Diaminosulphoanthraquinone-2-carboxylic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 261885. Compare this vol., i, 1206).—1 : 4-*Diaminoanthraquinone-2-carboxylic acid*, dark blue, glistening, bronze needles, m. p. 350° (about), is obtained from 2-amino-5-acetylamino-4-carboxybenzoyl-*o*-benzoic acid (this vol., i, 621) ; the *sulphate* forms brownish-red needles ; when heated with anhydrous boric acid (1 part) and 6 parts of fuming sulphuric acid (5% SO_3) at 190° and subsequently at 130—140° with the addition of 1 part of sulphuric acid (50% SO_3), it gives rise to 1 : 4-*diaminosulphoanthraquinone-2-carboxylic acid sulphate* as a brownish-red, crystalline precipitate.   F. M. G . M

Oxonium and Alkali Salts of Fluorones. HANS VON LIEBIG (*Ber.*, 1913, **46**, 2736—2745).—The composition of the chloride of fluorescein trimethyl ether-ester [Kehrmann and Scheunert's (A., 1910, i, 407) methyl 3 : 6-dimethoxy-9-phenylxanthonium-2'-carboxylate] varies according to the treatment to which it is subjected.   When prepared by the author's method (this vol., i, 865) and kept for five days at the ordinary temperature, a methyl-alcoholic solution of the chloride deposits fluorescein dimethyl ether of m. p. 198°; after removal of the latter compound, the addition of ether precipitates a *chloride*, $2C_{23}H_{20}O_6,3HCl,MeOH,2H_2O$, which has m. p. 110—125° (decomp.), and on crystallisation from water has the composition $C_{23}H_{20}O_6,HCl,MeOH,2H_2O$.   The above chlorides resemble those previously described in yielding with 33% aqueous potassium hydroxide a blue *o*-quinonoid potassium salt. The hydrate, $C_{23}H_{20}O_6,H_2O$, obtained by acidifying an aqueous solution of the potassium salt with acetic acid, probably has the constitution represented in formula II. (*loc. cit.*, 867).   On treatment with water the potassium salt yields a substance, $C_{23}H_{20}O_6$, which was previously considered to be a trimethyl ether-ester of fluorescein. The same substance is obtained by treating the potassium salt with methyl alcohol. It crystallises from cold methyl alcohol in slender, white needles, which sinter at 105—110° and gives off vapour at 126°, and again at a temperature a little above

180°; by warm methyl alcohol it is transformed into fluorescein dimethyl ether. It does not yield blue salts with alkalis, and therefore must contain the pyrone ring. It probably has the annexed constitution (I, where X = OMe).
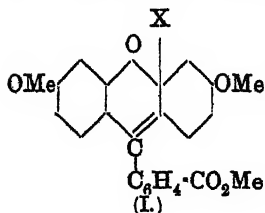
Solutions of the preceding methoxy-compound and the hydrate mentioned above, in 10—15% hydrochloric acid, deposit a *chloride*, which melts with evolution of gas at 150°, then solidifies, and has m. p. 205°. This chloride differs from the chlorides of fluorescein trimethyl ether-ester already described in being practically insoluble in water. It yields blue salts with alkalis and probably has the formula I (X = Cl).

By heating the disodium salt of fluorescein with methyl sulphate and shaking the product with ether and ammonia, the author has obtained a substance, m. p. 255°, which he considered to be a dimethyl ether of fluorescein (A., 1912, i, 381). The same substance is formed by treating the chloride of fluorescein trimethyl ether ester with strong aqueous ammonia. When pure it has m. p. 256—257°, and is stable towards boiling alcoholic hydrogen chloride and potassium hydroxide. Its constitution is now represented by formula II.
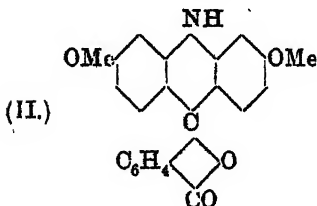
By the action of ammonia on a methyl-alcoholic solution of the chloride of fluorescein trimethyl ether-ester, Loth (*Diss.*, Lausanne, 1913) has obtained a substance, m. p. 257°, which he considers to be identical with the compound just mentioned, and to have the following structure:

$$NH\left[CO\cdot C_6H_4\cdot C(OMe)\!\!<\!\!{}^{C_6H_3(OMe)}_{C_6H_3(OMe)}\!\!>\!\!O\right]_2.$$
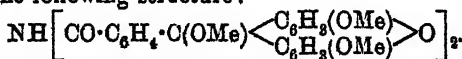
The stability of the author's compound towards alcoholic hydrogen chloride and potassium hydroxide is, however, not in agreement with this formula. It is possible that both substances are formed in the action of ammonia on the chloride; but that the particular compound isolated depends on the conditions under which the reaction is carried out and the method of working up the product.

In agreement with this view, the author finds that the action of ammonia on the product formed from ethyl sulphate and the disodium salt of fluorescein gives rise to two substances of m. p. 234° and 221°.

The former compound has been described previously (this vol., i, 80) as a diethyl ether of fluorescein, but is now considered to have a similar structure to that of the methyl compound represented in II, whilst the second *compound*, m. p. 221°, is presumably the ethyl analogue of Loth's compound.

When heated with acetic anhydride and sodium acetate, and the product treated with water, the chloride of fluorescein trimethyl ether-ester is partly converted into fluorescein dimethyl ether, of m. p. 198°. The dichloride of resorcinolbenzein dimethyl ether, when subjected to

same treatment, yields an *acetyl* derivative, $OAc \cdot CPh \begin{smallmatrix} C_6H_3(OMe) \\ C_6H_3(OMe) \end{smallmatrix} > O$, crystallising with benzene (1 mol.) in slender, colourless leaflets, which melt and lose their benzene at 110°, then solidify, and have m. p. 178°. This is converted by prolonged boiling with ethyl alcohol into the ethyl ether of m. p. 158°, the acetyl group being replaced by ethyl.

When shaken with ether and ammonia, the dichloride of resorcinol-benzein dimethyl ether yields a *substance*, which forms pale yellow crystals, m. p. 112—113°, and has the following structure:

$$OH \cdot CPh \begin{smallmatrix} C_6H_3(OMe) \\ C_6H_3(OMe) \end{smallmatrix} > NH.$$
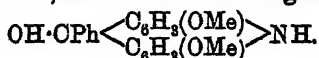
Evidence of the existence of eosin in various forms, corresponding with those of fluorescein (A., 1912, i, 379), has been obtained as follows : The chloride, formed by treating fluorescein with a hot mixture of alcohol and hydrochloric acid, is brominated in alcoholic solution and the resulting eosin fractionally extracted with methyl alcohol. The first extractions deposit a dark red eosin, the later fractions a reddish-white or flesh-coloured modification, whilst the residue is either reddish-white or orange. When heated, the eosin from the later fractions acquires a red colour at 200°, then becomes almost white at a temperature below 300°, and finally turns red again and melt at 304—305°. On crystallisation from benzene, the light-coloured eosin separates as a mixture of colourless, yellow and red prisms. The red variety probably corresponds with the red multi-molecular modification of fluorescein, the light-coloured form to the yellow unimolecular fluorescein, and the colourless variety to the lactone-form.

When boiled with aqueous alcoholic potassium hydroxide, the light-coloured eosin yields intensely violet or blue solutions. The addition of sulphuric acid to these solutions precipitates a brown substance, which on extraction with boiling chloroform leaves an eosin of the composition $2C_{20}H_8O_5Br_4,CHCl_3$ as a reddish or bluish-white, crystalline residue. The latter compound differs from ordinary eosin in giving a deep violet coloration with strong sulphuric acid, and in yielding with aqueous alkalis deep blue solutions having a green fluorescence ; when kept, the blue solutions slowly become violet and finally red. It loses its chloroform at 185—186°, and then dissolves in alkalis with a red colour. Attempts to isolate the blue salt formed by warming the compound with 33% aqueous potassium hydroxide were unsuccessful ; instead of the blue salt a brownish-red *tripotassium* salt, $C_{20}H_5O_5Br_4K_3$, was obtained.

Hydroxyquinolbenzein, to which Kehrmann has assigned formula III, yields with aqueous alcoholic potassium hydroxide a *tripotassium* salt IV, which separates in brownish-red crystals of the composition $C_{19}H_{19}O_5K_3,EtOH,H_2O$.

(III.)   (IV.)
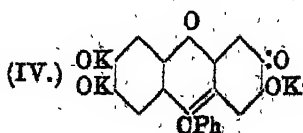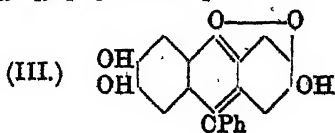
The author considers that the constitution of hydroxyquinolbenzein is best represented by a quinonoid structure, similar to that given above for the potassium salt, and thus avoids the assumption that the betaine-linking is stable towards alkalis, or that transformation into the quinonoid form occurs.   F. B.

Oxidation with Oxygen in Presence of Metallic Osmium. I. RICHARD WILLSTÄTTER and EUGEN SONNENFELD (*Ber.*, 1913, **46**, 2952—2958).—Unsaturated substances alone or diluted with acetone are agitated in special flasks with a small quantity of metallic osmium, prepared by igniting osmium ammonium chloride in a current of hydrogen, in an atmosphere of oxygen. The other metals of the platinum group do not act as oxygen-carriers under these conditions, but tellurium is active, although less so than osmium. A detailed account of the oxidation of *cyclo*hexene by this method is given ; the products are Δ²-*cyclo*hexenol, Δ¹-*cyclo*pentenealdehyde, much adipic acid, and a little adipoin (*cyclo*hexan-2-ol-1-one).

The first two were separated by converting the *cyclo*hexenol into the *naphthylurethane*, m. p. 156°, which crystallises in needles from alcohol or ethyl acetate on cooling its solution in either. Adipoin gives a p-*nitrophenylhydrazone*, m. p. 146° (decomp.), which crystallises from boiling alcohol in orange-red, hexagonal leaflets.   T. A. H.

Action of Light on the Colour Changes of Aldehyde Phenylhydrazone Solutions. HANS STOBBE and ROBERT NOWÁK (*Ber.*, 1913, **46**, 2887—2902).—The change of colour of solutions of the phenylhydrazones of benzaldehyde, cuminaldehyde, anisaldehyde, piperonaldehyde, and acetaldehyde on exposure to light has been investigated. In all cases the change is extremely sensitive to the action of light. Acid solutions are much more quickly affected than neutral solutions. The change is not due, as supposed by Baly and Tuck (T., 1907, **91**, 1572), to photo-isomerisation of the hydrazones to azo-compounds, but it is an oxidation process which takes place slowly in the dark and is greatly accelerated by light. The colour changes of other hydrazones and of osazones is likewise attributed to oxidation.

Benzaldehydephenylhydrazone is oxidised to dibenzylidenediphenyl-hydrotetrazone, whilst in no case were azo-compounds formed.
                                                                E. F. A.

Halogenated Alicyclic Ketones. II. Monohalogenides of Penta-, Hexa-, and Hepta-cyclic Ketones. ARTHUR KÖTZ, K. BLENDERMANN, E. KÁRPÁTI, and RICHARD ROSENBUSCH (*Annalen*, 1913, **400**, 47—54. Compare Kötz and Steinhorst, A., 1911, i, 210).—When *cyclo*pentanone, 1 : 4-dimethyl*cyclo*hexan-3-one, and *cyclo*hepta-none are halogenated by Kötz and Götz's method (A., 1908, i, 173), chlorine or bromine is substituted most easily in dimethyl*cyclo*hexanone and least readily in *cyclo*pentanone. The chloro-ketones are stable in the absence of light, but the bromo-ketones decompose very easily. 2-*Chloro*cyclopentanone, b. p. 76—77°, 2-*bromo*cyclopentanone, b. p. 79—82°/15 mm., 2-*chloro*cyclo*heptanone, b. p. 95°/13 mm., 2-*bromo*-cyclo*heptanone, b. p. 103°/13 mm., and 2-*chloro*-1 : 4-dimethyl*cyclo*hexan-3-one, b. p. 108—109°/15 mm., are described.   C. S.

α-**Hydroxy-ketones of the** *cyclo***Hexanone and** *cyclo***Heptanone Series.** ARTHUR KÖTZ, K. BLENDERMANN, RICHARD ROSENBUSCH, and E. SIRRINGHAUS (*Annalen*, 1913, **400**, 55—72).—Comparative experiments on the hydrolysis of 2-chloro*cyclo*pentanone, 2-chloro*cyclo*-hexanone, and 2-chloro*cyclo*heptanone by aqueous alkali carbonates or hydrogen carbonates show that *cyclo*pentan-2-olone cannot be thus obtained, that 2-chloro*cyclo*hexanone is readily hydrolysed by aqueous potassium carbonate in the cold, and that the formation of *cyclo*heptan-2-olone in satisfactory yield requires the action of boiling concentrated potassium carbonate for six hours. *cyclo*Hexan-2-ol-1-one, m. p. 98°, forms a *benzoyl* derivative, m. p. 122—123°, *semicarbazone*, m. p. 238°, *oxime*, m. p. 102—103°, *methyl ether*, m. p. 162°, and *ethyl ether*, m. p. 137° (which is converted into the methyl ether by warm methyl alcohol). *cyclo*Heptan-2-ol-1-one, m. p. 28°, unlike *cyclo*hexan-2-ol-1-one, possesses acidic properties and forms a *potassium* derivative. It forms a *methyl ether*, b. p. 65—66°/12 mm., but not a semicarbazone or oxime. The ethers of *cyclo*hexan-2-olone also do not form oximes or semicarbazones, and 2-hydroxy*cyclo*-hexanoneoxime cannot be etherified; the group

$$OR\cdot CH\cdot C\vdots NOH,$$
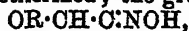
therefore, apparently cannot be formed.

2-Methoxy*cyclo*hexanone does not react with magnesium methyl iodide. *cyclo*Hexan-2-olone reacts only with difficulty, and yields ultimately *cyclo*hexanone (compare Sabatier and Mailhe, A., 1905, i, 706), whilst 1-methyl*cyclo*hexan-3-ol-2-one is similarly converted into 1 : 2-*dimethyl*cyclohexan-3-one, b. p. 178—179°.

*cyclo*Hexan-2-olone and its methyl and ethyl ethers react with phenylhydrazine in glacial acetic acid to form the same *osazone*, $C_{18}H_{20}N_4$, m. p. 150—151°, red crystals. *cyclo*Hexan-2-olone and its methyl ether are oxidised to adipic acid by alkaline potassium permanganate, and to glutaric acid by boiling nitric acid, D 1·22 ; the oxidation of the methyl ether is effected much less readily in both cases.

It is well known that hydroaromatic cyclic ketones condense with aldehydes except when a methyl group is present in the ortho-position to the carbonyl group. Hydroxyl and methoxy-groups apparently exert a similar inhibiting influence, because *cyclo*hexanolone or its methyl ether does not condense with benzaldehyde or cinnamaldehyde in the presence of alcoholic sodium hydroxide. 2-Methoxy-*cyclo*hexanone, however, reacts with sodium and amyl formate in ether to form, after acidification of the product, 2-*methoxy*-6-*hydroxymethyl-enecyclohexanone*, $C_8H_{12}O_3$, b. p. 98—100°/11 mm. (*semicarbazone*, m. p. 212—215°).

1 : 4-*Dimethyl*cyclohexan-2-ol-3-one, $C_8H_{14}O_2$, b. p. 91°/13 mm. (*benzoyl* derivative, m. p. 162°), is obtained by boiling 2-chloro-1 : 4-dimethyl*cyclo*hexan-3-one with saturated aqueous potassium carbonate, or, in a similar manner, from ethyl 2-chloro-1 : 4-dimethyl*cyclo*-hexan-3-one-4-carboxylate. Since the last compound, being produced by the chlorination of ethyl 1:4-dimethyl*cyclo*hexan-3-one-4-carboxylate by Kötz and Götz's method, must contain the chlorine atom in position 2 (compare Kötz and Steinhorst, A., 1911, i, 210), it follows, from the

production of 1 : 4-dimethyl*cyclo*hexan-2-ol-3-one by the hydrolysis of both chlorinated substances, that 2-chloro-1 : 4-dimethyl*cyclo*hexan-3-one (preceding abstract) must have this constitution, not that of the 4-chloro-isomeride. The chlorination of ethyl 1-methyl-4-*iso*propyl*cyclo*-hexan-3-one-4-carboxylate yields *ethyl 2-chloro-1-methyl-4-isopropyl-cyclohexan-3-one-4-carboxylate*, by the hydrolysis of which 2-*hydroxy*-1-*methyl*-4-*isopropyl*cyclo*hexan-3-one*, b. p. 139°/17 mm., is obtained.

<div align="right">C. S.</div>

Unsaturated Cyclic Ketones. Δ^2-*cyclo*Hexenone and Δ^2-*cyclo*-Heptenone (Tropilene). ARTHUR KÖTZ, K. BLENDERMANN, F. MÄHNERT, and RICHARD ROSENBUSCH (*Annalen*, 1913, **400**, 72—86).— Comparative experiments on the production of unsaturated cyclic ketones from the α-halogenated saturated ketones prove that hydrogen iodide is most readily, and hydrogen chloride is least readily, eliminated, and that the difficulty of eliminating hydrogen haloid increases from halogen-*cyclo*pentanones to halogen-*cyclo*heptanones. Aniline or trimethylamine is the most suitable eliminating reagent; to avoid the formation of hydroxy-ketones, water must not be present.

Willstätter's tropilene is identical with Δ^2-*cyclo*heptenone, obtained by the action of aniline on 2-bromo*cyclo*heptanone; it forms an *oxime*, m. p. 80—88°, and yields *cyclo*heptanone by reduction by Paal's method.

1 : 4-*Dimethyl*-Δ^1-cyclohexen-3-one, $C_8H_{12}O$, b. p. 75°/19 mm., is obtained by heating 2-hydroxy-1 : 4-dimethyl*cyclo*hexan-3-one with anhydrous oxalic acid at 110°. *Ethyl* 1 : 2-*dimethyl*-Δ^1-cyclohexen-3-one-6-carboxylate, $C_{11}H_{16}O_3$, b. p. 144—146°/13 mm. (*semicarbazone*, m. p. 202°; *oxime*, m. p. 109—110°), obtained by the action of methyl iodide and sodium ethoxide on ethyl 1-methyl-Δ^1-*cyclo*hexen-3-one-6-carboxylate, yields *ethyl* 1 : 2-*dimethyl*cyclohexan-3-one-6-carboxylate, b. p. 256—258° (*semicarbazone*, m. p. 210—211° [decomp.]), by reduction by Paal's method, and is converted into 1 : 2-*dimethyl*-Δ^1-cyclo-*hexen-3-one*, b. p. 118—119°/12 mm. (*semicarbazone*, m. p. 225° [decomp.]), by hydrolysis by alcoholic potassium hydroxide and distillation in a vacuum of the resulting acid. 1 : 2-Dimethyl-Δ^1-*cyclo*hexen-3-one is reduced to the corresponding saturated *ketone*, b. p. 84°/11 mm. (*semicarbazone*, m. p. 203—204°), by Paal's method, and yields γ-acetyl-butyric acid by oxidation by aqueous potassium permanganate at 0—6°.

<div align="right">C. S.</div>

Zinc Chloride as a Condensing Agent. III. Auto-condensation of Anils. G. REDDELIEN (*Ber.*, 1913, **46**, 2712—2717).—The author has shown previously (A., 1910, i, 118, 746) that acetophenone condenses with aniline in the presence of aniline zincichloride as a catalyst, yielding acetophenoneanil, together with a small quantity of a yellow substance, m. p. 98—99°. The by-product is now found to be dypnoneanil, and is formed by the auto-condensation of acetophenone anil. If the condensation is carried out at 180—190° a better yield of the substance is obtained. It was observed that in all cases in which dypnoneanil was formed as a by-product, the aniline zincichloride used as a catalyst underwent slight decomposition into zinc hydroxide, and

this suggested the possibility that the aniline hydrochloride, simultaneously produced by this decomposition, was the prime factor in the further condensation of acetophenoneanil to dypnoneanil. This view has been confirmed by heating acetophenoneanil for a few minutes with aniline hydrochloride, when a 60% yield of dypnoneanil was obtained ; under the same conditions, using aniline zincichloride, the acetophenoneanil remains unchanged.

If the heating is more prolonged and the temperature higher, 1 : 3 : 5-triphenylbenzene is formed. Exposure to air at the ordinary temperature also causes the transformation of acetophenoneanil into dypnoneanil, the condensation in this case being probably due to traces of hydrochloric acid in the air, for in closed vessels the acetophenoneanil may be kept for a long time without undergoing change.

Miller and Plöchl (A., 1896, i, 609) have already pointed out that there exists a very close resemblance in the reactions of aldehydes and ketones on the one hand, and of their anils on the other. In emphasising this analogy, the author refers to the similarity in the autocondensation products of acetophenone and its anil, and to the similar behaviour of aldehydes and their anils towards organo-magnesium compounds (Busch, A., 1904, i, 663; 1905, i, 519).

Further, anils closely resemble ketones and aldehydes in their behaviour toward phenylhydrazine and semicarbazide : thus, benzophenoneanil and acetophenoneanil readily react with these compounds in alcoholic solution to form the semicarbazones and phenylhydrazones of the corresponding aldehydes.

Finally, the ability of unsaturated and aromatic aldehydes to form coloured additive compounds with strong acids is shared by anils; fluoroneanil and dypnoneanil yield additive compounds with hydrogen chloride which are coloured respectively red and reddish-yellow, and are rapidly resolved by water into their components.

Dypnoneanil, $CMePh:CH\cdot CPh:NPh$, forms lustrous, light yellow, glassy prisms, m. p. 98—99°, and gives an intensely yellow coloration with sulphuric acid. It has also been obtained, together with acetophenoneanil, by heating dypnone and aniline in the presence of aniline zincichloride; if aniline hydrochloride is used as a condensing agent, triphenylbenzene is produced.

Dypnone-p-tolil, prepared from dypnone and aniline, using p-toluidine zincichloride as a catalyst, has m. p. 110°. It is accompanied by acetophenone-p-tolil, which crystallises from alcohol in yellowish-white needles, m. p. 31°. F. B.

Catalytic Action of Hydrogen Haloids in Condensations. I. Preparation of Ketoneanils. G. REDDELIEN (*Ber.*, 1913, **46**, 2718—2723. Compare preceding abstract).—In the preparation of ketoneanils by the condensation of aromatic ketones with amines, hydrogen haloids or their salts with aromatic amines may often be employed as catalysts in place of zinc chloride or amine zincichlorides previously used. Thus, benzophenoneanil is readily obtained by heating benzophenone and aniline at 170° in the presence of one drop of hydrochloric acid.

The reaction proceeds more rapidly than when the zinc salts are

employed, but is not so general in its application. Methyl ketones, such as acetophenone and $\alpha\beta$-unsaturated ketones, do not yield anils by this method, although the latter are readily obtained when aniline zincichloride is employed.

With respect to the mechanism of the reaction the author considers that the ketones first combine with the amines in the presence of hydrochloric acid to form compounds of the type OH·CRR·NHR,HCl, which lose water when heated, yielding hydrochlorides of the anils, CRR:NR,HCl; the anils, however, are very feeble bases in comparison with the amines, and, therefore, are liberated from their hydrochlorides by the action of the unchanged amines, the hydrochlorides of the latter compounds thus being regenerated.

It is pointed out that the hydrogen haloids may act as catalysts in opposite directions accordingly as they ionised or not. Whilst unionised hydrogen haloids act as catalysts in the condensation of ketones with amines, in the ionised state they accelerate the decomposition of the anils into their components and thus exert a catalytic action in the opposite direction.

In addition to benzophenoneanil, the following anils were obtained by heating the necessary ketones and amines in the presence of a little hydrochloric acid : phenyl α-naphthyl-ketoneanil, m. p. 93—94° (compare Busch and Falco, A., 1910, i, 747); benzildianil, m. p. 142°; benzophenone-p-tolil, crystallising from alcohol in long, stout, lustrous prisms, m p. 48° (compare Reddelien, A., 1910, i, 118); benzophenone-α-naphthil (Pauly, this Journ., 1877, ii, 614), which has m. p. 137·5°, and gives a blood-red coloration with strong sulphuric acid; fluorenoneanil (A., 1910, i, 746), the *hydrochloride* of which is precipitated in blood-red needles by passing hydrogen chloride into a benzene solution of the anil.   F. B.

Certain Substituted Benzalacetophenones [Phenyl Styryl Ketones]. FRANZ KUNCKELL and MARTIN HAMMERSCHMIDT (*Ber.*, 1913, **46**, 2676—2680. Compare Kunckell and Fürstenberg, A., 1912, i, 118).—*2-Hydroxy-5-acetylaminophenyl 2-nitrostyryl ketone*, golden-brown needles, m. p. 205° (decomp.), is obtained when aqueous sodium hydroxide is gradually added to an alcoholic solution of 2-hydroxy-5-acetylaminoacetophenone and o-nitrobenzaldehyde and the mixture neutralised after some time with dilute sulphuric acid, the temperature being maintained at about 20° during the whole operation. It is somewhat unstable, and decomposes when preserved for a short time. The preparation of the corresponding dibromide and flavone could not be effected.

2-Hydroxy-5-acetylaminophenyl 4-nitrostyryl ketone,

$$\text{OH·C}_6\text{H}_3(\text{NHAc})\text{·CO·CH:CH·C}_6\text{H}_4\text{·NO}_2,$$
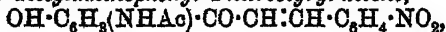
red, microcrystalline powder, m. p. 204°, is prepared in a similar manner from 2-hydroxy-5-acetylaminoacetophenone and p-nitrobenzaldehyde. It absorbs bromine in chloroform solution, yielding the corresponding *dibromide*, yellow needles, m. p. 125°, after previous softening, from which the flavone could not be obtained by the action of alcoholic potassium hydroxide.

2-Hydroxy-5-acetylaminophenyl 4-chlorostyryl ketone, golden needles,

m. p. 174°, and *2-hydroxy-5-acetylaminophenyl 2-hydroxystyryl ketone*, yellow crystals, m. p. 134°, are similarly formed from their components. In these cases, complete condensation can only be effected by heating the mixture on the water-bath. In neither case could the corresponding dibromide be obtained.

2-Hydroxy-5-acetylaminophenyl 4-methylstyryl ketone forms yellowish-white needles, m. p. 185°. It combines with bromine in chloroform solution to yield *2-hydroxy-5 acetylaminophenyl αβ-dibromo-β-p-tolyl-ethyl ketone*, m. p. 162°.

Terephthalaldehyde condenses with *2-hydroxy-5-acetylaminoaceto-phenone*, yielding a yellow *substance*, m. p. 217°, the constitution of which has not been definitely determined.   H. W.

Metal Ketyls, a Large Class of Substances with Tervalent Carbon. WILHELM SCHLENK and ALEXANDER THAL (*Ber.*, 1913, **46**, 2840—2854. Compare A., 1911, i, 545).—Phenyl diphenylyl ketone was dissolved in dry ether in an atmosphere of nitrogen, and the boiling point of the solution determined. This remained unchanged on the addition of a piece of bright potassium, indicating that potassium phenyl diphenylyl ketone has the formula

$$Ph \cdot C_6H_4 \cdot CPh(OK) -.$$
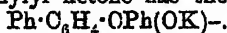
When a suspension of benzpinacone in benzene is mixed with a concentrated, alcoholic sodium ethoxide solution, sodiobenzophenone is formed, as indicated by the unstable, dark blue coloration. The sodium salt of the benzpinacone at first formed is dissociated immediately into the free radicles with a tervalent carbon atom, $CPh_2(ONa)-$. The name metal ketylen is proposed for such compounds containing tervalent carbon.

Special apparatus is described for their filtration, isolation, and for drying them in a current of nitrogen.

The sparingly soluble ketyls cannot be prepared in the manner described, since the surface of the metal becomes coated with a film of insoluble ketyl which prevents further action.

In such cases the ketone (dimethylpyrone) is mixed with the very soluble potassium phenyl diphenylyl ketone, when the insoluble ketyl (red potassiodimethylpyrone) separates out. Ether, benzene or pyridine may be used as solvents, but the two latter are more difficult to remove from the ketyl. Potassium, sodium, and lithium react equally well; magnesium in the form of amalgam also reacts with diaryl ketones.

Potassiodimethylpyrone forms a bright red powder, which oxidises so readily that it glows on exposure to the air.

Potassiochromone yields a deep orange-red product, and contains a further molecule of chromone. It chars on exposure.

Potassioxanthone separates together with a molecule of xanthone as deep blue needles.

*Potassio β-benzpinacolin*, $CPh_2:CPh \cdot OK-$, forms dark cubic crystals with a brown surface reflex.

Potassiophthalophenone is dark red.

Potassio-N-methylisatin separates in deep blue flakes.

Potassio-O-methylisatin forms a deep violet precipitate.

Potassio-m-*dibenzoylbenzene*, $COPh \cdot C_6H_4 \cdot CPh \cdot OK-$, forms a dark red powder.

Potassio-p-*dibenzoylbenzene* forms a additive compound with two molecules of potassium per molecule ; a deep red precipitate is formed, and the solution becomes deep red. The alternative ketyl (I) and quinonoid (II) formulæ are considered, but the latter is rejected,

$$-CPh(OK) \cdot C_6H_4 \cdot CPh(OK)- \qquad CPh(OK) \vdots C_6H_4 \vdots CPh(OK)$$
$$\text{(I.)} \qquad\qquad\qquad \text{(II.)}$$
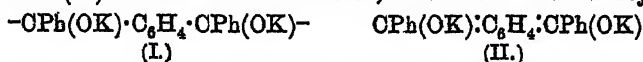
since the compound behaves like the other ketyls and glows on exposure to the air.

Potassiobenzil, $-CPh(OK) \cdot CPh \vdots O$, is obtained as a violet-coloured precipitate.

Potassiofuril is a black or bluish-black substance.

Potassiophenanthraquinone, $C_6H_4 {<}{\overset{CO-}{\underset{C_6H_4}{}}}{>}C(OK)-$, is dark brown.

Potassio-p-*benzoquinone* possesses a quinhydrone structure combining with a molecule of quinone ; it forms a deep bluish-green compound.

When o-benzoquinone is mixed with potassium phenyl diphenylyl ketyl, a dark green precipitate is formed, which soon becomes colourless, and is then potassiocatechol. When the ketyl solution is added slowly to the quinone, a precipitate is formed, and the solution becomes an intense reddish-violet ; this is attributed to the formation of the metal ketyl.

On adding diphenyl ketone to the potassium phenyl diphenylyl ketyl an intense violet-red coloration is produced. Excess of the ketyl causes a separation of a compound containing 1 atom of potassium to 2 molecules of diphenyl ketone. The red compound could not be isolated ; it possibly has the composition $CPh_2 \vdots C(OK)-$.

The atomic groups OK, ONa are considered to exhaust practically the entire valency force of the atoms to which they are attached.

E. F. A.

Preparation of Arylidoquinones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 262180).—*Di*-p-*chloroanilinobenzoquinone*, a yellowish-brown powder, m. p. over 300°, is obtained by heating together quinol and *p*-chloroaniline in the presence of ammoniacal copper oxide.

Bromoanilinonaphthaquinone is prepared in a similar manner from *p*-bromoaniline and α-naphthaquinone.   F. M. G. M.

Preparation of 1 : 4-Diaminoanthraquinone and its Derivatives, or of Sulphonic Acids of these Compounds. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 260899. Compare A., 1904, i, 512; 1905, i, 447; 1909, i, 243).—The preparation of aminoanthraquinones from aminobenzoyl-*o*-benzoic acids has previously been recorded, and that of 1 : 4-diaminoanthraquinones from 2-amino-5-acetylaminobenzoyl-*o*-benzoic acid, or its lactam (this vol., i, 621), is now described ; the operation is carried out at 190—200° with either 95% or fuming sulphuric acid ; under the latter conditions, especially in the presence of boric acid, sulphonated products are also formed. 2 : 5-*Diaminobenzoyl*-o-*benzoic acid*, yellow

crusts, which melt at 185° with conversion into the *lactam*, can also be employed in this reaction.

1 : 4-*Diamino-2-methylanthraquinone*, dark violet, glistening, bronze needles, m. p. 252°, is obtained from 2 : 5-diamino-*p*-toluoyl-*o*-benzoic acid, whilst 4-chloro-2-amino-5-acetylaminobenzoylbenzoic acid gives rise to 2-*chloro*-1 : 4-*diaminoanthraquinone*, dark violet needles, m. p. 234°. F. M. G. M.

Replacement of the Sulphonic Acid Group by Halogens in Hydroxyanthraquinonesulphonic Acids. GUSTAV HELLER [with SIEGFRIED SKRAUP (*Ber.*, 1913, **46**, 2703—2711).—Kelbe's method (A., 1883, 806 ; compare also Ullmann and Ochsner, A., 1911, i, 489, and Schilling, this vol., i, 493) of replacing the sulphonic acid group by chlorine or bromine, by the action of these elements on sulphonic acids in aqueous solution, has been applied by the author to the preparation of halogen derivatives of alizarin and anthrachrysone from the corresponding sulphonic acids.

3-Bromo-1 : 2-dihydroxyanthraquinone (D.R.-P. 77179 and 78643) is obtained in a pure condition by the addition of an aqueous solution of potassium bromide and bromate to sodium alizarin-3-sulphonate, acidified with sulphuric acid, and maintained at 95°. It crystallises in rosettes of brownish-red needles, m. p. 260—261°, yields a pale yellow *diacetyl* derivative, m. p. 204—205°, and dissolves in dilute aqueous alkali hydroxides, yielding bluish-violet solutions ; concentrated solutions of the hydroxides precipitate the corresponding alkali salts.

3-Chloro-1 : 2-dihydroxyanthraquinone, prepared by passing chlorine into a hot aqueous solution of alizarin-3-sulphonic acid, has m. p. 270—271°, and on benzoylation in pyridine solution yields a *dibenzoyl* derivative, m. p. 184°, together with a red *substance*, m. p. above 300°.

When dissolved in an ice-cold mixture of sulphuric and nitric acids, it is oxidised to 3-*chloro*-1 : 2 : 4-*trihydroxyanthraquinone*, m. p. 242—244°.

Nitration in glacial acetic acid solution yields 3-*chloro-4-nitro*-1 : 2-*dihydroxyanthraquinone*. This crystallises in orange-yellow needles, which become dark red and decompose slightly at 220°, then acquire a lighter colour, and finally melt at 285°.
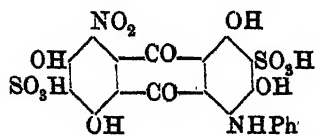
3-*Chloro-4-anilino*-1 : 2-*dihydroxyanthraquinone*, prepared by heating the preceding nitro-compound in aqueous sodium carbonate solution with aniline, crystallises in black needles or plates, m. p. 223—224°.

A solution of anthrachrysone in 33% aqueous sodium hydroxide deposits a lustrous, vivid red *sodium* salt, which is converted by ammonium chloride into the *ammonium* salt.

1 : 3 : 5 : 7-Tetrahydroxyanthraquinone-2 : 6-disulphonic acid, prepared by heating anthrachrysone with an excess of fuming sulphuric acid, forms a *sodium* salt, $C_{14}H_6O_6(SO_3Na)_2$, crystallising in glistening, coppery platelets (compare D.R.-P. 70803). On treatment with bromine in dilute acetic acid solution, the sodium salt is converted into 2 : 4 : 6 : 8-tetrabromo-1 : 3 : 5 : 7-tetrahydroxyanthraquinone, which forms lustrous, dark red needles, m. p. above 300°, and yields a sparingly soluble *ammonium* salt.

2 : 6-*Dibromo*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone*, prepared by brominating anthrachrysone in glacial acetic acid solution, crystallises in orange-red needles, m. p. above 290°, and also forms a sparingly soluble *ammonium* salt.

2 : 6-*Dichloro*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone* is obtained in lustrous, orange, silky needles by the addition of sodium hypochlorite to an aqueous solution of the sodium salt of anthrachrysone. The action of chlorine on 1 : 3 : 5 : 7-tetrahydroxyanthraquinone-2 : 6-disulphonic acid yields 4 : 8-*dichloro*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone*-2 : 6-*disulphonic acid.*

8-*Nitro* - 4 - *anilino* - 1 : 3 : 5 : 7 - *tetra-hydroxyanthraquinone* - 2 : 6 - *disulphonic acid* (annexed formula) is obtained in the form of its *trisodium* salt (dark blüish-violet crystals of a coppery lustre) by heating a solution of 4 : 8-di-nitro - 1 : 3 : 5 : 7 - tetrahydroxyanthra - quinone in aqueous sodium carbonate with aniline.

A similar replacement of the nitro-group by the aniline residue occurs when 4 : 8-dinitro-1 : 3 : 5 : 7 - tetrahydroxyanthraquinone (D.R.-P. 71964) is heated with aqueous sodium carbonate and aniline. The 8-*nitro*-4-*anilino*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone* thus formed crystallises in blackish-blue needles of a coppery lustre.

An account of the tinctorial properties of the above dyes is given.

F. B.

Preparation of a Menthol Ester. ROBERT MEYER (D.R.-P. 261228).—*Menthylglycine hydrochloride*, slender needles, is obtained when a fused suspension of glycine (20 parts) in menthol (70 parts) is treated with continual agitation at about 100° with dry hydrogen chloride and the product purified by crystallisation from water ; the free *base*, an oil, is decomposed by warm alkaline hydroxides, and with mercuric chloride furnishes a sparingly soluble *mercury* derivative.

F. M. G. M.

Scission of Racemic Amino-acids by means of Active Acids. I. AMEDEO COLOMBANO and GIUSEPPE SANNA (*Atti R. Accad. Lincei,* 1913, [v], **22,** ii, 234—237).—A solution containing equimolecular quantities of *d*-camphorsulphonic acid and glycine deposits a salt, $C_{12}H_{21}O_6NS$, which forms long, hygroscopic prisms, m. p. 165—173°, $[\alpha]_D + 14.69°$ (in 10·664% aqueous solution). Alanine similarly yields a camphorsulphonate, m. p. 105—110°, $[\alpha]_D^{18} + 14.33°$ (in 12·153% aqueous solution). These salts, however, yield racemic products when they are decomposed. Similar results were obtained under many different conditions, and no better success was obtained by substituting *d*-bromocamphorsulphonic acid.

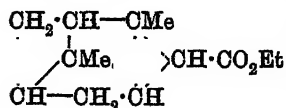Racemic salts were also produced from leucine and tyrosine in the same way.

R. V. S.

dl-α-Pinene and Ethyl Diazoacetate. EDUARD BUCHNER and KURT REHORST (*Ber.,* 1913, **46,** 2680, 2687. Compare Buchner and Weigand, this vol., i, 376—887).—The application of ethyl diazo-

acetate to the study of the constitution of *dl*-pinene leads the authors to the conclusion that the latter contains an endocyclic double bond and a methyl group directly attached to a carbon atom having a double bond. This is in conformity with Wagner's formula for pinene.

Pure *dl*-pinene was prepared from American turpentine by subjecting the latter to the action of nitrosyl chloride, the product formed being subsequently decomposed by boiling aniline.

A solution of ethyl diazoacetate in a little *dl*-pinene is slowly added to a mixture of the latter substance and copper powder at 160—165°; nitrogen is violently evolved, and, on distillation, *ethyl* 1:6:6-*trimethyl*-[0,1,4$^{5·7}$,1]-*tricyclo*-*octane-2-carboxylate* (annexed formula), b. p. 135°/12·5 mm., is obtained. Since, however, when suspended in alkali it immediately decolorises permanganate, it is probably contaminated with ethyl fumarate. When saponified with methyl-alcoholic potassium hydroxide, it yields 1 : 6 : 6-*trimethyl*-[0,1,4,$^{5·7}$,1]-tricyclo*octane*-2-*carboxylic acid*, crystalline powder, m. p. 165°, which is stable towards permanganate. The *silver* and *barium* salts were prepared, the latter being readily soluble in water. The *amide*, colourless leaflets, has m. p. 181°. Oxidation by potassium permanganate in hot acid solution converts the acid into a mixture of products from which terebic acid, m. p. 175°, separates after some time. Two other acids can be separated from the residue by converting them into their methyl esters. One of these crystallises in large prisms, whereas the other remains liquid. The latter, when saponified, yields an *acid*, m. p. 211—212°, which could not be further identified on account of its small amount. The former gives methyl*cyclo*propane-1 : 2 : 3-tricarboxylic acid, which has m. p. 192°, and does not evolve carbon dioxide at 220°. The identity of this substance is further established by comparison of its methyl ester, m. p. 76·5°, with a synthetically prepared specimen of the same substance (Buchner and Dessauer, A., 1894, i, 347).

The action of ethyl diazoacetate on pinene in the presence of copper powder has been previously investigated by Loose (A., 1909, i, 463), who obtained an oily product which, on saponification, yielded a non-crystallisable substance. This result is attributed to lack of uniformity in the pinene.

The authors have also studied the action of ethyl diazoacetate on *d*-pinene ($a_D + 39·8°$ in 1-dcm. tube) and have obtained a product which, when saponified, yields an acid, colourless needles, m. p. 123°, together with very small quantities of an isomeric acid, m. p. about 165°. With *l*-pinene ($a_D - 31·1°$ in 1-dcm. tube), on the other hand, the main product is the acid, m. p. about 165°, whilst only small amounts of the substance, m. p. about 123°, are obtained. The complete separation of the two acids is difficult, and it is suggested that the acid, $C_{13}H_{18}O_2$, m. p. 123°, is derived from nopinene present in crude optically-active oil of turpentine. H. W.

Bornylene Ozonide. CARL HARRIES and REINHOLD HAARMANN (*Ber.*, 1913, **46**, 2595—2596).—By the action of washed, 8% ozone on

bornylene in hexane solution, the *ozonide*, $C_{10}H_{16}O_3$, was obtained as a white precipitate, which gradually decomposed after some time, but was fairly stable towards boiling water. In order to hydrolyse the product, bornylene was saturated with ozone in glacial acetic acid and the solution heated for thirty minutes. The solvent was then evaporated under reduced pressure and the residue distilled, when a pale yellow oil, containing a dialdehyde, b. p. 90—110°/16 mm., and a solid, b. p. 125—150°/18 mm., containing in all probability an aldehydic acid, were obtained.   ·   J. C. W.

Research on the Eucalypts of Tasmania and their Essential Oils. RICHARD T. BAKER and HENRY G. SMITH (*Reprint* from the *Proc. Roy. Soc. Tasmania*).—Oils distilled from leaves of the various species of eucalyptus occurring in Tasmania have been examined with a view to ascertain their composition and economic value, and of using some of the data thus obtained as a guide in deciding certain outstanding taxonomic problems in connexion with the genus. The results show that the twenty-one species found in Tasmania may be divided into groups as follows:

   I. Eight species yielding oils containing over 50% cineole, much pinene, but no phellandrene or piperitone. The characters of the oils from these species are as follows: *Eucalyptus cordata*, D_{15}^{15} 0·9138, a_D +9·3°, n_D^{18} 1·4965, saponification number 14·8, soluble in 1·25 vols. of 70% alcohol; contains cineole 62%, *d*-pinene, and esters. *E. Muelleri*, D_{15}^{15} 0·9096, a_D +10·4°, n_D^{24} 1·4629, saponification number 15·3, soluble in 4 vols. of 70% alcohol; contains cineole 60%, *d*-pinene, and esters. *E. Perriniana*, D_{15}^{15} 0·9119, a_D +8·9°, n_D^{15} 1·4651, saponification number 10·3, soluble in 2 vols. of 70% alcohol; contains cineole 68%, *d*-pinene, esters, and sesquiterpene. *E. Rodwayi*, D_{15}^{15} 0·9075, a_D +10·6°, n_D^{24} 1·4653, saponification number 3·9, soluble in 6 vols. of 70% alcohol; contains cineole 64%, *d*-pinene, and sesquiterpene. *E. unialata*, D_{15}^{15} 0·9179, a_D +3·1°, n_D^{15} 1·4690, saponification number 11·1, soluble in 1·75 vols. of 70% alcohol; contains cineole 62%, *d*-pinene, esters, and sesquiterpene. *E. urnigera*, D_{15}^{15} 0·9088, a_D +11·8°, n_D^{22} 1·4638, soluble in 5 vols. of 70% alcohol; contains cineole 63%, *d*-pinene, and esters. *E. vernicosa*, D_{15}^{15} 0·9038, a_D +11·3°, n_D^{18} 1·4651, saponification number 5·9, soluble in 1 vol. of 80% alcohol; contains cineole 59%, and *d*-pinene. *E. globulus*, as already frequently recorded.

   II. Two species yielding oils containing cineole from 25—50%, as well as pinene and phellandrene. *E. Gunnii*, D_{15}^{15} 0·9014, a_D +1·5°, n_D^{18} 1·4752, saponification number 6·7, soluble in 4 vols. of 80% alcohol; contains cineole 41%, *d*-pinene, phellandrene, esters, and sesquiterpene. *E. viminalis*, D_{15}^{15} 0·9154, a_D +4·2°, n_D^{19} 1·4711, saponification number 9·5, soluble in 1 vol. of 80% alcohol; contains 50% cineole, *d*-pinene, phellandrene, esters, and sesquiterpene.

   III. Two species yielding oils with over 50% cineole, phellandrene largely replacing pinene, and piperitone being present. *E. linearis*, D_{15}^{15} 0·9096, a_D −10·2°, n_D^{24} 1·4659, saponification number 5·8, soluble in 6 vols. of 70% alcohol; contains cineole 52%, with phellandrene, piperitone, and sesquiterpene. *E. Risdoni*, D_{15}^{15} 0·9045—0·9145, a_D −0·3° to 14·6°, n_D 1·4660 (at 19°) to 1·4733 (at 16°), saponification

number 21·3—27, soluble in 1·25—5 vols. of 70% alcohol; contains cineole 56—58%, phellandrene, piperitone, and esters.

IV. Seven species yielding oils containing much phellandrene, less than 25% of cineole, and having piperitone present. *E. amygdalina*, D_{15}^{15} 0·8668—0·8848, a_D − 59·1° to − 75·1°, n_D^{18} 1·4761—1·4790, saponification number 2·9—3·2, soluble in 7 vols. of 70% alcohol; contains cineole 12—24%, phellandrene, piperitone and sesquiterpene. *E. coccifera*, D_{15}^{15} 0·8810, a_D − 35·8°, n_D^{24} 1·4831, saponification number 4·9, insoluble in 10 vols. of 80% alcohol; contains cineole less than 5%, phellandrene, piperitone and eudesmol. *E. Delegatensis*, D_{15}^{15} 0·8664, a_D − 48·4°, n_D^{24} 1·4828, saponification number 3·1, insoluble in 10 vols. of 80% alcohol; contains traces of cineole, and is chiefly composed of phellandrene with some piperitone and sesquiterpene. *E. regnans*, D_{15}^{15} 0·8802—0·8879, a_D − 28·4° to 31·1°, n_D^{20} 1·4882—1·4901, saponification number 13·2—15·4, soluble in 5 vols. of 80% alcohol; contains phellandrene, eudesmol, piperitone, esters, sesquiterpene and traces of cineole. *E. taeniola*, D_{15}^{15} 0·8864, a_D − 27·6°, n_D^{17} 1·4872, saponification number 3·2, soluble in 5 vols. of 80% alcohol; contains cineole 7%, phellandrene, piperitone, eudesmol and sesquiterpene. *E. virgata*, D_{15}^{15} 0·8883, a_D − 20·9°, n_D^{18} 1·4819, saponification number 3·3, soluble in 3 vols. of 80% alcohol; contains cineole 21%, phellandrene, piperitone, eudesmol and sesquiterpene. *E. obliqua*, D_{15}^{15} 0·8836—0·8845, a_D − 24·2° to 28·8°, n_D 1·4839 (at 19°) to 1·4852 (at 24°), saponification number 7·2—8·1, soluble in 3—4 vols. of 70% alcohol; contains phellandrene, aromadendral, less than 5% of cineole and no piperitone.

The two remaining species do not fall readily into any of the above groups. *E. acervula*, D_{15}^{15} 0·8956, a_D − 1·1°, n_D^{18} 1·4756, saponification number 32·8, soluble in 1 vol. of 80% alcohol; contains cineole 21%, *d*-pinene, phellandrene, geraniol, geranyl acetate, liquid and solid paraffins, sesquiterpene. *E. phlebophylla*, D_{15}^{15} 0·8925, a_D − 22·4°, n_D^{18} 1·4761, saponification number 3·2, insoluble in 10 vols. of 80% alcohol; contains cineole 9%, *l*-pinene, phellandrene and eudesmol.

The cineole was determined by the resorcinol method.   T. A. H.

The Presence of the 8-Carbon Ring in Normal Caoutchoucs. CARL HARRIES (*Ber.*, 1913, 46, 2590—2595. Compare this vol., i, 286).—The author has succeeded in degrading Para caoutchouc to *cyclo*octane-1 : 5-dione. The caoutchouc regenerated by heating the dihydrochloride with pyridine (this vol., i, 380) was converted into the diozonide in ethyl acetate solution, and the residue, after removing the solvent under reduced pressure, was heated for an hour with water at 125°. The filtrate was then neutralised with calcium carbonate, filtered, evaporated in a vacuum, and extracted twenty times with ether. The extract was distilled, and the fraction b. p. 60—90°/14 mm. contained chiefly lævulinaldehyde, the fraction b. p. 100—125°/14 mm. partly solidified and contained *cyclo*octane-1 : 5-dione, and the fraction b. p. 180—200°/14 mm. deposited non-aldehydic crystals, m. p. 88°. The syrup of calcium salts was acidified and extracted with ether, and the extract distilled. The products included much formic and lævulic acids and an oily ketonic acid, b. p. 160—180°/14 mm.

The fraction containing *cyclo*octane-1 : 5-dione was redistilled, and the pale yellowish-green distillate, b. p. 107—110°/14 mm., was found to solidify in ice to large, colourless leaflets. It was difficult to remove the last traces of lævulinaldehyde, so the *disemicarbazone*, $C_{10}H_{18}O_2N_6$, was prepared. It forms a white, crystalline mass, m. p. 186·5°.

The variety of products shows that the regenerated caoutchouc consists of a mixture of at least three forms, due to the displacement of the double linkings in the 8-ring, but the formation of so much lævulinaldehyde and acid indicates that a large part of the caoutchouc is regenerated in its natural form. The degradation into *cyclo*butane-1 : 5-dione is represented by the scheme :
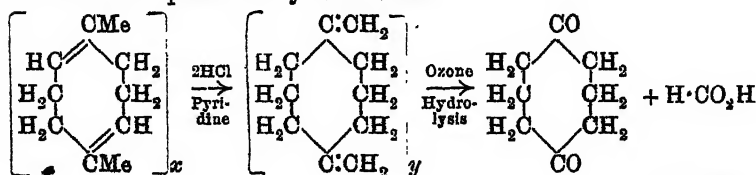
J. C. W.

Estimation of Free Sulphur in Vulcanised Caoutchouc. PAUL BARY (*Rev. gen. Chim. pure appl.*, 1913, **16**, 142—145).—Polemical against Alexander (this vol., i, 67), and in agreement with Hinrichsen and Kindischer (A., 1912, i, 706).   F. M. G. M.

New Glucosamine Compound and the Constitution of Chitin. YASHIRO KOTAKE and YOSHITA SERA (*Zeitsch. physiol. Chem.*, 1913, **88**, 56—72).—α- and β-Modifications of *lycoperdin*,

$$C_{18}H_{24}O_9N_2,$$

are obtained from the fungus *Lycoperdon gemmatum*. Both show the biuret and iodine reactions and reduce Fehling's solution : they occupy a mean position between the polypeptides and polysaccharides.

α-Lycoperdin is insoluble in water and crystallises in characteristic, granular crystals, $[a]_D$ − 6·7°, changing to − 5·28°. It becomes black at 240°. β-Lycoperdin forms a soluble sulphate crystallising in needles.

On hydrolysis, 90% of glucosamine and 14% of formic acid are obtained, equivalent to the formation of two molecules of glucosamine and one molecule of formic acid. Constitutional formulæ are assigned to lycoperdin and to chitin, which is assumed to contain four glucosamine molecules, in all of which the NH_2 group is acetylated. The carbon to which the amino-group is attached is supposed to be directly joined to the potentially aldehydic carbon in the next molecule.

E. F. A.

Application of the Bio-chemical Method to Gentiana acaulis, L. Isolation of a New Glucoside; Gentiacaulin. MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], **8**, 241—250).—Investigation of a purified alcoholic extract of *Gentiana acaulis* showed that it contained products hydrolysable by both invertase and emulsin, and in addition a new glucoside, which is not attacked by emulsin, which was isolated and characterised. No gentiopicrin was present.

The new glucoside, *gentiacaulin*, $C_{47}H_{60}O_{29}$, crystallises from hot alcoholic extracts of the plant in transparent, golden-yellow needles, has no definite melting point, but decomposes from 145° to 160°, and is lævorotatory, $[a]_D - 63.84°$ in water. It is precipitated by lead subacetate solution, gives an unstable green coloration with ferric chloride, and reduces Fehling's solution on boiling. It is hydrolysed by boiling dilute sulphuric acid, yielding xylose and *gentiacaulein*, m. p. 177°, crystallising in bright yellow needles, soluble in alcohol or ether, and dissolving in alkalis to give solutions which rapidly become dark brown on exposure to air. T. A. H.

Gitonin, a New Digitalis Glucoside. ADOLF WINDAUS and A. SCHNECKENBURGER (*Ber.*, 1913, **46**, 2628—2633).—Merck's "digitonin" (compare Kiliani, A., 1911, i, 139) is not an individual substance, but contains another glucoside to which the name gitonin is applied. The solubilities of the two substances in alcohol vary considerably with the strength of the solvent. *Gitonin*, $C_{49}H_{80}O_{23}$, is less soluble in 95% alcohol, but more soluble in 85% alcohol, than digitonin, and was obtained in white, amorphous granules when a solution of 100 grams of crude material in 3 litres of 95% alcohol was left for some weeks. It decomposes at 272°, has $[a]_D^{20} - 50.69°$, and gives a rose-red to wine-red coloration on boiling with concentrated hydrochloric acid. It forms an *additive* compound, $C_{76}H_{126}O_{24}$, with cholesterol, in sparingly soluble, small, slender needles, and a similar *compound*, $C_{79}H_{130}O_{24}$, with stigmasterol (compare digitonin compounds, A., 1909, i, 172).

After hydrolysis with alcoholic hydrochloric acid, water caused the crystallisation of *gitogenin*, $C_{26}H_{42}O_4$, which was obtained pure after many recrystallisations, in the form of white, narrow leaflets, m. p. 271—272°. It is indifferent towards hydroxylamine, but forms a *diacetyl* derivative, long needles, m. p. 243—244°, a *dipropionyl* derivative, long, narrow leaflets, 195—196°, and yields on oxidation with chromic acid, a dibasic *acid*, $C_{26}H_{40}O_6$, m. p. 242—243°, the *methyl* ester of which crystallises in leaflets, m. p. 145—146°. The sugar syrup did not readily crystallise, although it contained much galactose. The presence, in addition, of 21% of pentoses agrees with the equation : $C_{49}H_{80}O_{23} + 4H_2O = C_{26}H_{42}O_4 + 3C_6H_{12}O_6 + C_5H_{10}O_5$.
J. C. W.

Mustard Oil Glucosides. II. **Glucocheirolin.** WILHELM SCHNEIDER and LUDWIG A. SCHÜTZ (*Ber.*, 1913, **46**, 2634—2640. Compare A., 1912, i, 1007).—The isolation of the glucoside, glucocheirolin, from wallflower seeds is described. The crude substance was obtained from the dry, fat-free seeds by extraction with several large portions of alcohol which had been dried over sodium. The different fractions contained products in which the proportion, K : S : N, varied, but approached more and more to the expected value 1 : 3 : 1. The very hygroscopic glucoside was then dissolved in water, clarified by shaking with litharge, then quickly treated with lead acetate, and filtered. After precipitating the dissolved lead and exactly neutralising, the solution was concentrated in a vacuum and stirred into absolute alcohol. The precipitate

was then recrystallised a few times from much 90% alcohol, and finally obtained in small, colourless needles, m. p. 158—160°.

Glucocheirolin, $C_{11}H_{20}O_{11}NS_2K,H_2O$, only parts with water after some days in a hot exhausted desiccator over phosphoric oxide. It is tasteless, has $[a]_D^{27}$ — 21·56° to — 21·09°, and gives up one molecule of sulphuric acid on boiling with acidified barium chloride. When silver nitrate is added to the dilute solution, the cheirolin silver sulphate separates after a time as a jelly, in which crystal-centres slowly appear, and finally small, feathery needles, $C_5H_9O_2NS_2,Ag_2SO_4,H_2O$, decomp. 154°, are deposited. The behaviour of glucocheirolin is similar to that of sinigrin and accords with the constitution :

$$SO_2Me \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot N(O \cdot SO_3K) \cdot S \cdot C_6H_{11}O_5.$$
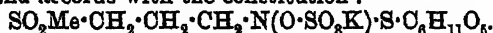
<div align="right">J. C. W.</div>

Derivatives of a- and β-Bromopicrotoxinins. PAUL HORRMANN (*Ber.*, 1913, **46**, 2793—2801).—The author now finds that picrotoxinin really has the old formula, $C_{15}H_{16}O_6$, not $C_{14}H_{16}O_6$ (A., 1912, i, 709).

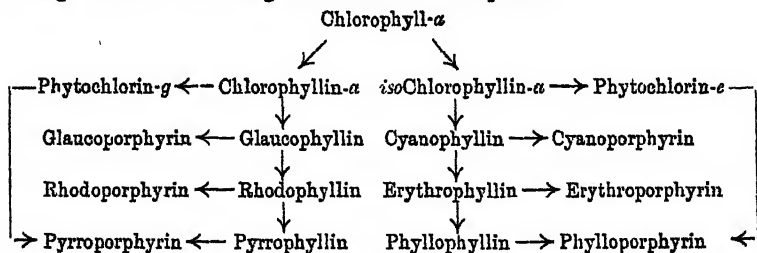By treatment with boiling aqueous potassium hydroxide and subsequent acidification, a-bromopicrotoxinin yields an *acid*,

$$C_{15}H_{17}O_7Br,$$
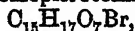
m. p. 248° (decomp.), needles containing H_2O or prisms, $[a]_D^{17\cdot5}$ — 28°51' in alcohol (*c* = 2·889) (*methyl* ester, m. p. 218°, $[a]_D^{17\cdot5}$ — 29°21'; *ethyl* ester, crystals, $[a]_D^{17\cdot5}$ — 31°59'), a boiling alcoholic solution of which is reduced by zinc dust and aqueous ammonium chloride to *a-picrotoxininic acid*, $C_{15}H_{18}O_7$, m. p. 209° (decomp.), $[a]_D^{17\cdot5}$ — 4°53' in alcohol (*c* = 5·981). a-Picrotoxininic acid reacts additively with bromine, reduces alkaline potassium permanganate in the cold and Fehling's solution and ammoniacal silver oxide solution by heating, and neutralises 1 mol. of sodium hydroxide at the ordinary temperature and 2 mols. on the water-bath. It forms a *methyl* ester, m. p. 182°, $[a]_D^{17\cdot5}$ — 9°44' in alcohol (*c* = 1·970), and *ethyl* ester, m. p. 159°, $[a]_D^{17\cdot5}$ — 8°4' (*c* = 4·238) ; its potassium salt reacts with aqueous bromine to form an *acid*, $C_{15}H_{17}O_7Br,H_2O$, m. p. 236° (decomp.), $[a]_D^{17\cdot5}$ — 58°2' in alcohol (*c* = 3·532). By reduction with palladous chloride and hydrogen at 2 atmospheres, a-picrotoxininic acid yields *a-dihydropicrotoxininic acid*, $C_{15}H_{20}O_7$, m. p. 232° (decomp.), $[a]_D^{17\cdot5}$ — 4°10' in alcohol (*c* = 2·006), which is also a lactonic acid, since it neutralises one mol. of alkali in the cold and 2 mol. on the water-bath. By boiling with 2N-sulphuric acid, a-picrotoxininic acid is converted into an isomeride, *β-picrotoxininic acid*, $C_{15}H_{18}O_7$, m. p. 235° (decomp.), $[a]_D^{17\cdot5}$ — 48° in alcohol (*c* = 9·254) (*methyl* ester, m. p. 204°, $[a]_D^{17\cdot5}$ — 50°3' in alcohol [*c* = 1·049]; *ethyl* ester, m. p. 198°, $[a]_D^{17\cdot5}$ — 49°57' in alcohol [*c* = 2·436]), which is stable to aqueous bromine, does not reduce Fehling's solution or ammoniacal silver oxide solution, and neutralises only 1 mol. of alkali on the water-bath.
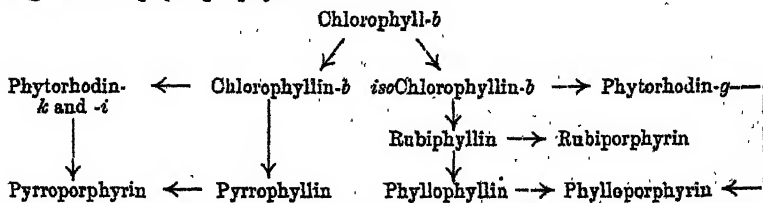
<div align="right">C. S.</div>

Chlorophyll. XXII. Degradation of the two Components of Chlorophyll by Alkalis. RICHARD WILLSTÄTTER, MAX FISCHER, and LENNART FORSÉN (*Annalen*, 1913, **400**, 147—181. Compare A., 1908, i, 198 ; 1910, i, 126 ; 1911, i, 392).—The monocarboxylic acids,

phyllophyllin and pyrrophyllin, obtained as the final products of the action of alcoholic potassium hydroxide on chlorophyll, are produced, not one from each component of the chlorophyll as might be expected, but both from each component. An explanation of this is to be found in Willstätter and Utzinger's lactam theory of the brown phase (A., 1911, i, 392). The first action of the alkali on, for example, chlorophyll-*a*, indicated in the colour phase, is rupture of the lactam group and its closure in another direction, yielding chlorophyllin-*a* (lactam group, ·CO·NH·, closed and the *a*- and β-carboxyl groups free) and *iso*chlorophyllin $\overset{\gamma}{a}$ (lactam group, ·CO·NH·, closed and β- and γ-carboxyl groups free); in the subsequent changes caused by the alkali, the lactam groups disappear and the β-carboxyl group is destroyed, so that the difference between phyllophyllin and pyrrophyllin is due probably to the different positions of the carboxyl groups *a* and γ.

Rapid hydrolysis of chlorophyll by hot alkalis yields mainly *iso*chlorophyllins *a* and *b* (from which phytochlorin-*e* and phytorhodin-*g* respectively are obtained by eliminating the magnesium by acids) ; in the cold, the chief products are chlorophyllin-*a* and -*b*, from which phytochlorin-*g* and the feebly basic phytorhodins-*k* and -*i* are respectively obtained by the action of acids. In the *a* series, every change shown in the diagram has been accomplished.

Chlorophyll-*a*

—Phytochlorin-*g* ← Chlorophyllin-*a*	*iso*Chlorophyllin-*a* → Phytochlorin-*e* —
Glaucoporphyrin ← Glaucophyllin	Cyanophyllin → Cyanoporphyrin
Rhodoporphyrin ← Rhodophyllin	Erythrophyllin → Erythroporphyrin
→ Pyrroporphyrin ← Pyrrophyllin	Phyllophyllin → Phylloporphyrin ←

The degradation of chlorophyll-*b* is more difficult, because the second oxygen atom must be reduced without any elimination of carbon dioxide occurring; this has been effected by means of concentrated methyl-alcoholic potassium hydroxide in the presence of pyridine, whereby even the very unstable phytorhodin-*g* has been degraded to phylloporphyrin.

Chlorophyll-*b*

Phytorhodin-*k* and -*i* ← Chlorophyllin-*b*	*iso*Chlorophyllin-*b* → Phytorhodin-*g*—
	Rubiphyllin → Rubiporphyrin
Pyrroporphyrin ← Pyrrophyllin	Phyllophyllin → Phylloporphyrin ←

The differentiation and identification of the preceding porphyrins have been effected by the partition method (between hydrochloric acid and ether).

Potassium iso*chlorophyllin*-a, $C_{34}H_{31}O_6N_4MgK_3$, a dark blue powder with a pale green streak, is obtained by boiling gently methylchlorophyllide-*a* with concentrated methyl-alcoholic potassium hydroxide for five minutes and, after further suitable treatment of the solution and dilution with water, adding potassium chloride. Its solutions, in contrast to those of chlorophyllin-*a*, are intensely fluorescent. By heating with pyridine (3 parts) and methyl-alcoholic potassium hydroxide (10 parts) at 150—155° in a silver autoclave for four or five hours, it yields the easily soluble *potassium* salt of the very unstable *cyanophyllin*, $C_{33}H_{34}O_4N_4Mg$. Cyanophyllin is a weaker acid than the isomeric glaucophyllin and is not extracted from ether by 0·003% aqueous ammonia. Its solutions are splendidly blue and intensely fluorescent. By treatment with strong hydrochloric acid it is converted into *cyanoporphyrin*, $C_{33}H_{36}O_4N_4$, reddish-brown needles.

Erythrophyllin, $C_{33}H_{34}O_4N_4Mg$, is prepared from chlorophyll-*a* by boiling with pyridine and methyl alcoholic potassium hydroxide and, after the hydrolysis, heating the alkaline mass in an autoclave at exactly 175—180°; the *potassium* salt, obtained by diluting with water, is then decomposed by sodium dihydrogen phosphate. Erythrophyllin crystallises in pointed rhombic plates, forms a *dimethyl* ester, $C_{35}H_{38}O_4N_4Mg$, long, red prisms, and has weaker acidic properties than rhodophyllin. It is converted into phyllophyllin by methyl-alcoholic potassium hydroxide at 200—210°. Mixtures of cyanophyllin, erythrophyllin, and phyllophyllin can be separated by treating the ethereal solution with 0·2% disodium hydrogen phosphate which extracts the strongest acid, cyanophyllin; somewhat concentrated disodium hydrogen phosphate or not too dilute aqueous ammonia then removes erythrophyllin, the phyllophyllin remaining in the ethereal solution.

Erythroporphyrin, $C_{33}H_{36}O_4N_4$, red, silky prisms, obtained by treating erythrophyllin with concentrated hydrochloric acid and a little ether, forms a *hydrochloride*, pale red needles (insoluble in dilute hydrochloric acid), and a *dimethyl* ester, $C_{35}H_{40}O_4N_4$, brown or reddish-brown prisms, the *hydrochloride* of which is easily soluble in hydrochloric acid.

Di- and mono-basic phyllins derived from the *b* component of chlorophyll are most readily obtained from methylchlorophyllide-*b*. This substance, dissolved in pyridine, is completely hydrolysed by gentle boiling for five minutes with methyl-alcoholic potassium hydroxide, and the blood-red, fluorescent, alkaline solution is heated at 150—155° (whereby an unstable *phyllin* is obtained, the solution of which in ether is green and in alcoholic alkali blue and fluorescent), and finally at 165—170° after dilution with more alcoholic potassium hydroxide. The product is now the *potassium* salt, bluish-violet crystals, of rubiphyllin, from which *rubiphyllin*, $C_{33}H_{34}O_4N_4Mg$, is obtained by treatment with sodium dihydrogen phosphate. Rubiphyllin, which is more easily obtained by hydrolysing methylphæophorbide-*b* or phytorhodin-*g* with methyl-alcoholic potassium hydroxide and heating the resulting solution with magnesium oxide at 170°, crystallises usually in triangular leaflets; its crystalline powder is bluish-black. Rubiphyllin, unlike erythrophyllin and rhodophyllin, is not extracted

from its ethereal solution by 0·5% disodium hydrogen phosphate, but is at once removed by a 1% solution; the *dipotassium* salt,

$$C_{33}H_{32}O_4N_4MgK_2,$$

is a violet powder, which reacts with methyl sulphate to form *rubiphyllin dimethyl* ester, $C_{35}H_{38}O_4N_4Mg$, olive-brown prisms. *Rubiporphyrin*, $C_{33}H_{36}O_4N_4$, obtained by dissolving the preceding potassium salt in 20% hydrochloric acid, crystallises in rhombic leaflets which are olive-brown, in transmitted light, and forms a *hydrochloride*, olive-brown prisms, and *dimethyl* ester, $C_{35}H_{40}O_4N_4$, violet prisms.

By heating with methyl-alcoholic potassium hydroxide above 170°, rubiphyllin is converted into phyllophyllin, which is identified as the characteristic calcium salt.

By hydrolysing a pyridine solution of methylchlorophyllide-*b* with methyl-alcoholic potassium hydroxide in the cold, chlorophyllin-*b* is obtained, but always accompanied with *iso*chlorophyllin-*b*; consequently, the degradation products of the former are always contaminated with the phyllins of the *iso*-series, the final products at 205—210° being pyrrophyllin and phyllophyllin. Pure pyrrophyllin can be obtained by hydrolysing methylphæophorbide-*b* by methyl-alcoholic potassium hydroxide in the cold, and heating the resulting alkaline solution with magnesium oxide in a silver autoclave; up to 200°, several still unknown phyllins are formed, but after heating for five hours at 220°, the product is pyrrophyllin, which is identified by conversion into pyrroporphyrin. The latter is obtained directly when phytorhodins-*i* and -*k* are heated at 205—210° with methyl-alcoholic potassium hydroxide alone.

Phytorhodins-i and -k, the latter usually predominating, are obtained together by several methods; the hydrochloric acid number of *k* is 14—14·5, of *i* 15—16, so that their separation requires very careful fractionation with 14% hydrochloric acid. The best method of preparing them is as follows. Chlorophyll (from stinging-nettle leaves) is kept in petroleum for a few weeks until allomerisation is complete. The solution is shaken with concentrated methyl-alcoholic potassium hydroxide until the hydrolysis of the chlorophyll is complete, and then with hydrochloric acid to remove the magnesium. The products are dissolved in ether, the more basic constituents are removed by repeated extraction with 13% hydrochloric acid, and finally the brown ethereal solution is treated with 14—14·5% hydrochloric acid to remove phytorhodin-*k*, and with 17% hydrochloric acid to separate phytorhodin-*i*; the substances require still further purification.

Phytorhodin-k, $C_{34}H_{84}O_6N_4$, black, metallic leaflets, and *phytorhodin*-i, $C_{34}H_{84}O_6N_4$, black, metallic leaflets, resemble one another in their solubilities, but give different colour reactions with potassium hydroxide, cæsium hydroxide, formic acid, and concentrated nitric acid.

By the term "hydrochloric acid" number of a chlorophyll derivative, the author denotes the percentage strength of the hydrochloric acid which is required to extract about 2/3 of the solute from the solution of the derivative in a volume of ether equal to that of the hydrochloric acid. A more rigidly defined number, however, is required for the differentiation of substances which have very nearly equal basicities. This is found in the "partition" number, which

represents the percentage amount of a substance extracted under definite conditions from ethereal solution by hydrochloric acid of a definite strength; the conditions are, 3 milligrams of substance, 1 litre of ether, and 100 c.c. of hydrochloric acid, the extraction lasting one minute. The concentration of the acid is either that denoted by the hydrochloric acid number, or, in the comparison of substances of different basicity, any other concentration suitable for the extraction.

The value of the partition number is illustrated by the comparison of phylloporphyrin and pyrroporphyrin; both have hydrochloric acid number 0·5, but the partition number of the former is about 35 and of the latter about 4.   C. S.

Chlorophyll. XXIII. Parent Substances of the Phyllins and Porphyrins. RICHARD WILLSTÄTTER and MAX FISCHER (*Annalen*, 1913, 400, 182—194).—Since the degradation of hæmin and of chlorophyll yields similar, but not identical, porphyrins, which, however, give identical products by oxidation (A., 1910, i, 499) and by reduction (A., 1912, i, 41), and since the dissimilarity of the porphyrins is possibly conditioned by differences in the position of the carboxyl groups, the elimination of the latter becomes a matter of prime importance. This has been accomplished with the phyllins and porphyrins derived from chlorophyll. The decarboxylation of chlorophyll derivatives by heating with methyl-alcoholic potassium hydroxide in a sealed tube proceeds only as far as the monocarboxylic acid, decomposition then beginning at 250° with the formation of hæmopyrrole and amorphous, brown products. Complete removal of carbon dioxide from the carboxyl groups, however, is effected by heating rapidly and carefully with soda-lime; the yields are small because the product decomposes at temperatures below the temperature of formation. Potassium rhodophyllin is mixed with soda-lime (free from iron), and is heated in small quantities rapidly and carefully by a naked flame until the colour changes suddenly from pale grey to brown. The mass is rapidly cooled, moistened with water, and extracted with warm ether. The ethereal solution is well washed with potassium hydroxide and with 5% hydrochloric acid. After washing finally with dilute ammonia and concentrating the ethereal solution, a *substance*, $C_{31}H_{34}N_4Mg$, m. p. about 205°, bluish-violet crystals, is obtained, which is called *aetiophyllin*, and is the parent of the phyllins. Aetiophyllin forms violet-red, intensely fluorescent solutions, and in ether is remarkably stable to 4—7% hydrochloric acid ; in petroleum, however, even 0·05% hydrochloric acid changes the colour of the solution to that of aetioporphyrin.

Porphyrins lose carbon dioxide much less readily than phyllins, so that the best method of preparing aetioporphyrin, the parent of the porphyrins, is by treating an ethereal solution of aetiophyllin with 20% hydrochloric acid, whereby the magnesium is at once replaced by hydrogen. *Aetioporphyrin*, $C_{31}H_{36}N_4$, m. p. about 280°, hydrochloric acid number 3, partition number for 3% hydrochloric acid 40 (compare preceding abstract), is obtained in violet, crystalline crusts, and forms a *styphnate*, $C_{31}H_{36}N_4,C_6H_3O_8N_3$. m. p. 170°, red prisms, by which it is best purified. It also forms a *hydrochloride*, olive-brown needles,

picrate, red prisms, *aurichloride* and *platinichloride*, and yields characteristic complex compounds with salts of the heavy metals.

Phylloporphyrin, pyrroporphyrin, and rhodoporphyrin when heated with soda-lime each yields aetioporphyrin, thus confirming Willstätter's theory that the two former are different because of the difference in the position of the carboxyl group.

Aetiophyllin can be obtained from aetioporphyrin by treating a concentrated ethereal solution of the latter with magnesium methyl iodide (Willstätter and Forsén, this vol., i, 499), and subsequently with sodium dihydrogen phosphate.
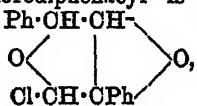
The absorption spectrum of aetiophyllin is very similar to that of pyrrophyllin, and that of aetioporphyrin to that of pyrroporphyrin, but contains much stronger bands.　　　　　　　　　　　　　C. S.

The Quantitative Dyeing of Silk with Basic Dyes. H. SALVATERRA (*J. pr. Chem.*, 1913, [ii], **88**, 502—504. Compare this vol., ii, 258).—Quantitative experiments on the dyeing of silk with a number of magenta-dyes show that the amount of these dyes taken up by the silk is proportional to their molecular weights, and thus supports the view that the dyeing of silk is a chemical process analogous to salt-formation.　　　　　　　　　　　　　　　　　F. B.

Constitution of the So-called α- and β-Halogendiphenacyls. OSKAR WIDMAN [with G. KARL ALMSTRÖM] (*Annalen*, 1913, **400**, 86—130).—The constitutions previously ascribed to the α- and β-halogendiphenacyls (A., 1909, i, 822) are withdrawn and are to be replaced by the following: α-chlorodiphenacyl is cis-2-*chloro*-3 : 4-

$$\begin{array}{c} \text{Ph·CH·CH–} \\ oxido\text{-}3:5\text{-}diphenyltetrahydrofuran, \quad \text{O} \diagdown \quad | \quad \diagup \text{O, and } \beta\text{-chloro-} \\ \text{Cl·CH·CPh} \end{array}$$

diphenylacyl is the corresponding trans-*isomeride*,

$$\begin{array}{c} \text{Ph·CH–CH–} \\ \text{O} \diagdown \quad | \quad \diagup \text{O} \\ \text{H·CCl·C·Ph} \end{array}$$
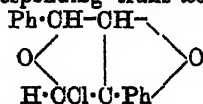
The evidence on which these constitutions are based is given below the most important proofs being furnished by the reactions of the α- and β-halogendiphenacyls with aniline and with hydrazine hydrate.

Paal and Demeler's statements, that only α-bromodiphenacyl results from the interaction of alcoholic sodium ethoxide and ω-bromoacetophenone and that the α-compound is changed to the β-isomeride by boiling alcohol, are incorrect. The authors show that α-chloro(or bromo-)-diphenacyl is unchanged by boiling alcohol, but that in the presence of sodium chloride and a little sodium hydroxide, it is converted almost quantitatively into the β-isomeride in twenty-four to forty-eight hours at the ordinary temperature. In the preparation of the halogendiphenacyls, therefore, both isomerides are formed, the amount of the β-compound being greater the longer the substances are kept in contact with the alcoholic, alkaline mother liquor. Since β-halogendiphenacyl can be converted indirectly into the α-compound (*loc. cit.*), the two compounds are most probably stereoisomeric.

β-Chlorodiphenacyl (*trans*-2-chloro-3 : 4-oxido 3 : 5-diphenyltetrahydrofuran) has m. p. 147—148°, not 154—155°, as stated in the literature.

The course of the reaction whereby ω-halogenacetophenones and alcoholic sodium ethoxide yield oxido-tetrahydrofurans is, in its first stage, probably analogous to those described by Darzens (A., 1905, i, 116) and by Claisen (A., 1905, i, 286), in which ketones or aldehydes condense with esters of halogenated fatty acids in the presence of sodium ethoxide or of sodamide to form esters of substituted glycidic acids : $2CH_2Cl \cdot COPh + NaOH = O{<}^{CH \cdot COPh}_{CPh \cdot CH_2Cl} + NaCl + H_2O$. The intermediate product then does not yield a four-membered ring by loss of hydrogen chloride, but is converted into a furan derivative, $O{<}^{CH-CHPh}_{CPh \cdot CHCl}{>}O$. The two suppositions in this explanation are supported by experimental evidence. With regard to the formation of the oxido-group, the authors find that ω-chloro- or bromo-acetophenone and benzaldehyde in the presence of alcoholic sodium ethoxide, in accordance with Darzen's statement that esters of halogenated fatty acids condense preferentially with aldehydes rather than with ketones, yield not a trace of a furan derivative, but a *substance*, m. p. 89—90°, which proves to be *α-benzoyl-β-phenylethylene oxide*, $O{<}^{CHPh}_{CH \cdot COPh}$.

The second supposition, that a ketone containing a halogen atom in the γ-position to the carbonyl group is capable of yielding a furan derivative, is supported by the behaviour of a substance described by Perkin (T., 1885, 47, 842) as phenyl ω-bromopropyl ketone; this substance, however, does not exhibit the properties of a ketone, and is most probably 2-bromo-5-phenyltetrahydrofuran.

By heating with a large excess of 99% hydrazine hydrate, α-chlorodiphenacyl (*cis*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran) is converted into a *substance*, $C_{16}H_{12}N_2$, m. p. 139—140°, faintly yellow, rhombic plates, which proves to be 3 : 5-diphenylpyridazine (Almström, this vol., i, 1240).

By treatment with boiling aniline, α-chlorodiphenacyl yields a *substance* (I.), $C_{22}H_{16}NCl$, m. p. 146—147°, faintly yellow plates, whilst β-chlorodiphenacyl (*trans*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran) yields a *substance* (II.), $C_{22}H_{17}ON$, m. p. 150°, citron-yellow needles, which forms yellow solutions with bluish-green fluorescence. The constitutions of the substances I. and II. were elucidated after the discovery (compare Almström, *loc. cit.*) that 1 : 3 : 5-triphenylpyrrol-2-one (which is isomeric with II.) is converted by phosphorus trichloride into 2-chloro-1 : 3 : 5-triphenylpyrrole (which is isomeric with I.), and by phosphorus pentachloride into 2 : 4-dichloro-1 : 3 : 5-triphenylpyrrole. Since the last substance is also formed by the action of phosphoric and phosphoryl chlorides on I., it follows that I. must be *4-chloro-1 : 3 : 5-triphenylpyrrole*. Substance II. is then easily proved to be *4-hydroxy-1 : 3 : 5-triphenylpyrrole*, since it forms an *acetyl* derivative, m. p. 132—133°, colourless needles, by treatment with aqueous sodium hydroxide and acetyl chloride in acetone at 0°, and is converted into I. (4-chloro-1 : 3 : 5-triphenylpyrrole) by phosphorus trichloride at 170—190°.

By treatment with warm acetic anhydride and a little concentrated sulphuric acid, 4-hydroxy-1:3:5-triphenylpyrrole or its acetyl derivative yields 4-*acetoxy*-2-*acetyl*-1:3:5-*triphenylpyrrole*,

$$\begin{matrix} OAc \cdot C \!\!-\!\!-\!\! CPh \\ \quad\;\;|| \qquad\qquad \rangle C \cdot COMe, \\ CPh \cdot NPh \end{matrix}$$
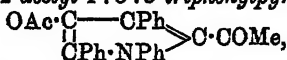
m. p. 189—190°, colourless needles, from which 4-*hydroxy*-2-*acetyl*-1:3:5-*triphenylpyrrole*, m. p. 180—181°, is obtained by hydrolysis with alcoholic sodium ethoxide.

4-Chloro-1:3:5-triphenylpyrrole is a very stable substance, and is not attacked by sodium amalgam, boiling alcoholic sodium ethoxide, nitrous acid, or boiling alkaline potassium permanganate. By treatment with boiling acetic anhydride and concentrated sulphuric acid, it yields 4-*chloro*-2-*acetyl*-1:3:5-*triphenylpyrrole*, $C_{24}H_{18}ONCl$, m. p. 136° (*semicarbazone*, m. p. about 236° [decomp.]), which reacts with benzaldehyde (1 mol.), 10% sodium hydroxide, and alcohol at the b. p. to form 4-*chloro*-2-*cinnamoyl*-1:3:5-*triphenylpyrrole*, $C_{31}H_{22}ONCl$, m. p. 197°, stout, yellow needles. By reduction with hydriodic acid, D 1·22, and amorphous phosphorus at 160°, 4-chloro-1:3:5-triphenylpyrrole yields 1:3:5-triphenylpyrrole, m. p. 150—151°, which reacts with boiling acetic anhydride and concentrated sulphuric acid to form 2(?)-*acetyl*-1:3:5-*triphenylpyrrole*, $C_{24}H_{19}ON$, m. p. 165—166°.

By treatment with methylaniline at 130—140°, α- and β chlorodiphenacyls yield, not pyrrole derivatives, but phenacylmethylaniline.

Now that the α- and β-halogendiphenacyls have been proved to be *cis*- and *trans*-2-halogen-3:4-oxido-3:5-diphenyltetrahydrofuran respectively, the nature of their additive compounds with halogen hydrides and acyl haloids (Paal and Stern, A., 1901, i, 154; Paal and Schulze, A., 1902, i, 229) is readily understood, and some inaccuracies in the statements of these investigators are easily detected. *trans*-2-Chloro-3:4-oxido-3:5-diphenyltetrahydrofuran and hydrogen chloride, best in warm glacial acetic acid, yield 2:3-*dichloro*-4-*hydroxy*-3:5-*diphenyltetrahydrofuran*, $O {\Large\langle}{\begin{matrix} CHPh \cdot CH \cdot OH \\ CHCl \cdot CPhCl \end{matrix}}$, m. p. 164° (decomp.), which is converted into 4-hydroxy-1:3:5-triphenylpyrrole and 4-*hydroxy*-3:5-*diphenyl*-1-*p-tolylpyrrole*, m. p. 152°, citron-yellow plates, by aniline and *p*-toluidine respectively on the water-bath. In a similar manner, *trans*-2-chloro-3:4-oxido-3:5-diphenyltetrahydrofuran and 12% hydrogen bromide in glacial acetic acid at about 30° yield 2-*chloro*-3-*bromo*-4-*hydroxy*-3:5-*diphenyltetrahydrofuran*, m. p. 155° (decomp.). The substance is given this constitution, not that of the 4-bromo-3-hydroxy-isomeride, because it loses only hydrogen bromide, not both hydrogen chloride and bromide by treatment with alcoholic sodium ethoxide. Contrary to the statement of Paal and his collaborators (*loc. cit.*), the substance, being a bromohydrin, obviously contains a hydroxyl group; the acetyl derivative, m. p. 89—90°, is obtained by the action of acetic anhydride and two drops of concentrated sulphuric acid. This acetyl derivative is identical with the additive compound (2-chloro-3-bromo-4-acetoxy-3:5-diphenyltetrahydrofuran) of β-chlorodiphenacyl and acetyl bromide described by Paal and his co-workers (*loc. cit.*). In a similar manner, the additive compound of β-bromodiphenacyl and hydrogen chloride (*trans*-3-chloro-2-bromo-4-hydroxy-

3 : 5-diphenyltetrahydrofuran) yields an acetyl derivative, m. p.
89—90°, identical with the additive compound of β-bromodiphenacyl
and acetyl chloride. Knowing the constitutions of β-chloro- and
bromo-diphenacyls, the author is able to assert that the two preceding
acetyl derivatives, in spite of their similarities in appearance and
m. p., are not identical, as stated by Paal (*loc. cit.*). The assertion is
proved, not only by a comparison of the corresponding propionyl and
valeryl derivatives which differ in m. p. (see below), but also by the
fact that by treatment with alcoholic sodium ethoxide, *trans*-3-chloro-2-
bromo-4-acetoxy-3 : 5-diphenyltetrahydrofuran (that is, the additive
compound of β-bromodiphenacyl and acetyl chloride) yields *trans*-3-
chloro-2-bromo-4-hydroxy-3 : 5-diphenyltetrahydrofuran, whilst *trans*-2-
chloro-3-bromo-4-acetoxy-3 : 5-diphenyltetrahydrofuran (the additive
compound of β-chlorodiphenacyl and acetyl bromide) is more exten-
sively changed and yields *cis*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetra-
hydrofuran (α-chlorodiphenacyl). In a similar manner, *trans*-2 : 3-
dichloro-4-acetoxy-3 : 5-diphenyltetrahydrofuran, prepared by the addi-
tion of acetyl chloride to β-chlorodiphenacyl or by treating *trans*-2 : 3-
dichloro-4-hydroxy-3 : 5-diphenyltetrahydrofuran with acetic anhydride
and concentrated sulphuric acid, is converted by alcoholic sodium
ethoxide into *trans*-2 : 3-dichloro-4-hydroxy-3 : 5-diphenyltetrahydro-
furan or *trans*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran, accord-
ing as 1 or 2 molecules of the ethoxide are used.

trans-3-Chloro-2-bromo-4-hydroxy-3 : 5-diphenyltetrahydrofuran (the
additive compound of β-bromodiphenacyl and hydrogen chloride) yields
the *propionyl* derivative, $C_{19}H_{18}O_3ClBr$, m. p. 106°, and the *valeryl*
derivative, m. p. 104—105°, by treatment with propionic anhydride
and valeric anhydride respectively in the presence of a little con-
centrated sulphuric acid. By similar treatment, *trans*-2-chloro-3-bromo-
4-hydroxy-3 : 5-diphenyltetrahydrofuran (the additive compound of
β-chlorodiphenacyl and hydrogen bromide) yields a *propionyl* derivative,
m. p. 69°, and *valeryl* derivative, m. p. 93°.

As stated by Paal and Schulze (*loc. cit.*), *cis*-2-halogen-3 : 4-oxido-
3 : 5-diphenyltetrahydrofurans (α-halogendiphenacyls) do not react with
halogen hydrides to form additive compounds (*cis*-2 : 3-dihalogen-
4-hydroxy-3 : 5-diphenyltetrahydrofurans) ; moreover, these substances
cannot be prepared by the action of sodium ethoxide on the *cis*-
2 : 3-dihalogen-4-acetoxy-3 : 5-diphenyltetrahydrofurans (additive com-
pounds of α-halogendiphenacyls and acetyl chloride).

Bromodeoxybenzoin, $CHBrPh\cdot COPh$, and bromopropiophenone,
$CHBrMe\cdot COPh$, by treatment with cold alcoholic sodium ethoxide
do not yield analogues of the α- and β-bromophenacyls ; the former is
converted into the benzoin, m. p. 131°, and the latter into an oily
substance which does not contain bromine.   C. S.

Conversion of Quinatoxines into Quinaketones and the
Reduction of these to the Alkaloids of Cinchona Bark. ADOLF
KAUFMANN and MAX HUBER (*Ber.*, 1913, **46**, 2913—2924). Rabe and
collaborators have shown (A., 1910, i, 417) that of the four asym-
metric carbon atoms in the chief cinchona alkaloids, that numbered 3
(*loc. cit.*) is the principal source of the isomerism among the alkaloids,

and have explained the apparent formation of a single ketone from each pair of isomerides (A., 1909, i, 252) by assuming that the ketone is tautomeric in each case. They have also shown (Abstr., 1911, i, 742) that cinchotoxine can be converted into cinchoninone and the latter reduced to cinchonine (A., 1908, i, 100), but the yield of the latter is very small, and no proof has been given that it is optically identical with natural cinchonine. The authors now show that in the conversion of cinchotoxine into cinchonine by Rabe's method, the reactions may be regarded as taking place (1) symmetrically, when two pairs of mirror-image isomerides will be formed in equal quantities, or (2) asymmetrically, when 4 optical isomerides will be formed in unequal quantities. They have applied this method to hydrocinchotoxine, and although the results are not conclusive, they indicate that it is the asymmetric direction which the reactions take, whence they conclude that hydrocinchoninone is not an equivalent mixture of two mirror-image isomerides.

Hydrocinchotoxine (hydrocinchonicine), prepared by von Miller and Rohde's method from hydrocinchonine, itself obtained by the reduction of cinchonine by von Skita's process, is an oil having $[a]_D^{23} + 8 \cdot 8°$ in dry alcohol; it yields a *benzoyl* derivative, m. p. 121—122°, which crystallises from light petroleum in colourless needles, and is sparingly soluble in ether. On treatment in hydrobromic acid with bromine vapour, hydrocinchotoxine yields *bromohydrocinchotoxine dihydrobromide*,

$$C_{19}H_{23}ON_2Br,2HBr,$$
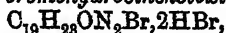
m. p. 198° (approx.), yellow crystals, readily soluble in water but sparingly so in alcohol, and this with sodium in an alcoholic solution of sodium ethoxide yields hydrocinchoninone, m. p. 130°, which shows mutarotation (compare Rabe, A., 1909, i, 253), and on reduction with palladium black in presence of hydrogen yields dihydrocinchonine (cinchotine), $[a]_D^{21} + 203 \cdot 4°$, as chief product with a smaller amount of dihydrocinchonidine, m. p. 231°, $[a]_D^{21} - 94 \cdot 6°$.

In like manner, hydroquinotoxine (hydroquinicine) was converted into *bromohydroquinotoxine dihydrobromide*,

$CH_3 \cdot CH_2 \cdot CH—CH—CH_2$
 |
 CH_2
 |
 CH_2
 |
$CH_2—NH—CHBr \cdot CO \cdot Q$
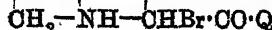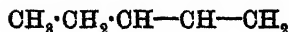
$C_{20}H_{25}O_2N_2Br,2HBr,H_2O,$

m. p. 178° (annexed formula, in which $Q = 6$-methoxyquinoline), and this into *hydroquininone*,

$$C_{20}H_{24}O_2N_2,$$
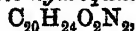
m. p. 98—99°, $[a]_D^{21}$, changing from $+83 \cdot 08°$ after twenty-four hours to $+73 \cdot 29°$ as the final value, which forms a mixture of needles, platelets, and crusts of yellow colour, and yields a *picrate*, m. p. 224°.

T. A. H.

Oxycolchicine. SIMON ZEISEL and A. FRIEDRICH (*Monatsh*, 1913, 34, 1181—1186).—*Oxycolchicine*, $C_{22}H_{23}(or_{25})O_7N$, m. p. 266—268°, obtained by oxidising colchicine with potassium pyrochromate and sulphuric acid, crystallises in faintly yellow, microscopic prisms; it is fairly soluble in hot alcohol and readily so in chloroform. Oxycolchicine gives a green colour passing into brown with sulphuric acid,

and with nitric acid a carmine-red changing to violet and brown. With boiling hydrochloric acid it appears to undergo changes quite similar to those given by colchicine. It is insoluble in cold potassium hydroxide solution, but gradually passes into solution on warming, methyl alcohol and acetic acid being split off. Oxycolchicine also reacts with hydroxylamine, but no definite derivative has been obtained. It is probable that in its formation from colchicine a $>CH_2$ group is converted into $>CO$. Formic and acetic acids were found as by-products of the oxidation. Further work on oxycolchicine will be undertaken by Windaus in continuation of his researches on the parent alkaloid (A., 1911, i, 904).   T. A. H.

Preparation of Alcoholic Methyl Ethers. J. D. RIEDEL (D.R.-P. 261588).—The following methyl ethers have been prepared from the corresponding alcohols in alkaline solution by means of methyl sulphate: benzyl methyl ether, methyl *isoamyl* ether, and borneol methyl ether; whilst the employment of methyl iodide gave rise to *γ-methylmorphimethine methyl ether*, leaflets, m. p. 259°; *δ-methylmorphimethine methyl ether*, needles, m. p. 277°; *methylcodeine methiodide*, glistening, colourless rods, decomp. 263°; *α-dimethylmorphimethine methiodide*, needles, decomp. 263°; *β-dimethylmorphimethine methiodide*, needles, m. p. 320—330°, and *cinnamyl methyl ether*, b. p. 115°/15 mm.   F. M. G. M.

Action of Acetal on Tetrahydropapaverine. AMÉ PICTET and STANISLAS MALINOWSKI (*Ber.*, 1913, 46, 2688—2697. Compare Pictet and Gams, A., 1911, i, 807).—The authors have studied the condensation of acetal with tetrahydropapaverine, in the hope that it would proceed on similar lines to the action of methylal on veratrylnorhydrohydrastinine, and thus yield one of the optically inactive corydalines. This does not appear to be the case. Two isomeric substances, which the authors name α- and β-coralydine, are obtained, which have the same composition as the coryladines, but differ from them in their properties.

When acetal is gradually added to a hot solution of tetrahydropaverine hydrochloride in hydrochloric acid, a mixture of hydrochlorides is obtained, which can be separated by cautious washing with water and subsequent fractional crystallisation from dilute hydrochloric acid.

In this manner, *α-coralydine hydrochloride*, m. p. 254°, and *β-coralydine hydrochloride*, m. p. 228—230°, are obtained.
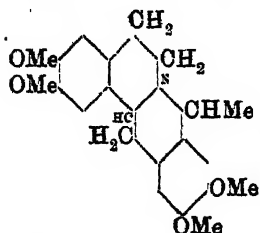
α-Coralydine (annexed formula), prepared by the addition of sodium carbonate to the above hydrochloride, forms colourless, shining leaflets, m. p. 148°. It gives a green coloration with warm, concentrated sulphuric acid. The following salts have been prepared: *sulphate*, m. p. 210°; *nitrate*, m. p. 242°; *picrate*, pale yellow needles, m. p. 134°; *aurichloride*, red crystals, m. p. 154°; *platinichloride*, yellow crystals, m. p. 246—247°. Attempts to resolve the base by quinic acid in alcohol solution and by

o-bromocamphorsulphonic acid in aqueous or alcoholic solution were unsuccessful.

When warmed with alcohol and iodine, α-coralydine yields *dehydro-coralydine*. The *hydriodide*, golden-yellow needles, m. p. 263°; *hydrochloride*, pale yellow needles, m. p. 230°; *nitrate*, yellow needles, m. p. 277—278°, and *aurichloride*, yellowish-brown needles, m. p. 252° (decomp.), of the base have been prepared. These salts differ greatly from the corresponding salts of dehydrocorydaline, from which the conclusion is drawn that the tetrahydro-derivatives, coralydine and corydaline, are structurally isomeric.

Oxidation of α-coralydine by potassium permanganate has been effected according to the directions of Dobbie and Lander for coryladine (T., 1894, **65**, 57; 1895, **67**, 17). The sole product appears to be *m*-hemipinic acid, which was identified by conversion into its ethylimide (Goldschmidt, A., 1889, 167). The latter consists of colourless needles (instead of pale yellow needles described by Goldschmidt), m. p. 229°.

β-Coralydine crystallises in colourless prisms, m. p. 115°. It gives a colourless solution in cold concentrated sulphuric acid, which becomes green when warmed. Oxidation with alcoholic iodine solution converts it into dehydrocoralydine, the identity of which, with the product obtained in a similar manner from α-coralydine, is established by comparison of the hydrochlorides, hydriodides and nitrates obtained from the two substances. From this it follows that α- and β-coralydines must be stereoïsomerides, and probably are related to one another in the same manner as the two inactive corydalines. H. W.

1. Polymeric Tetramethylenecarbamide. 2. Some Derivatives of Pyrrole. EMIL FISCHER (*Ber.*, 1913, **46**, 2504—2510).— In attempting to prepare ornithin by the combination of tetramethylene-diamine and carbon dioxide, it has been found that the base absorbs carbon dioxide with the formation of a substance which is apparently a carbamate; this, when heated for two days in a sealed tube at 230°, undergoes conversion into a colourless, sparingly soluble compound which commences to decompose at 260°. When heated with lime or in a sealed tube with hydrochloric acid, this substance, which is probably a polymeric form of *tetramethylenecarbamide*,

$$\begin{matrix} CH_2 \cdot CH_2 \cdot NH \\ CH_2 \cdot CH_2 \cdot NH \end{matrix} \!\!> CO,$$
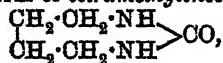
regenerates tetramethylenediamine.

Pyrrole-2 : 5-dicarboxylic acid (Ciamician and Silber, A., 1886, 938) in the form of the sodium salt is easily reduced by sodium amalgam with formation of a *pyrroline-2 : 5-dicarboxylic acid*, colourless prisms or needles, which becomes pink in the air and when heated commences to decompose at 235°.

2 : 5-Diacetyl-1-methylpyrrole, m. p. 133—134° (Ciamician and Silber, A., 1887, 843), is more readily obtained by the action of sodium hydroxide and methyl sulphate on 2 : 5-diacetylpyrrole than by the earlier process starting with 1-methylpyrrole. It can be oxidised by potassium permanganate followed by hydrogen peroxide to *1-methyl-pyrrole-2 : 5-dicarboxylic acid*, needles of no definite m. p.; *silver* salt,

colourless needles. This acid is possibly identical with a substance briefly described earlier (Bell, A., 1879, 525).

Pyrrolealdehyde (Bamberger and Djierdjian, A., 1900, i, 309) can be methylated in alkaline solution by methyl sulphate with production of 1-*methylpyrrole-2-aldehyde*, a colourless oil, b. p. 75—76° (corr.) /12—13 mm., which, unlike the inodorous unsubstituted aldehyde, has an odour resembling benzaldehyde; *phenylhydrazone*, an almost colourless, crystalline powder, m. p. 127—128°(corr.). Oxidation by silver oxide converts the aldehyde into 1-methylpyrrole-2-carboxylic acid, agreeing in m. p. with that described by Bell (*loc. cit.*); *silver* salt, sparingly soluble.   D. F. T.

Condensation of Ethyl Oxalate with Acetylpyrroles. Oskar Piloty and H. Will (*Ber.*, 1913, **46**, 2607—2612).—Acetyl-pyrroles condense with ethyl oxalate with elimination of alcohol, giving rise to coloured compounds which are closely related to the phono-pyrrolecarboxylic acids and, therefore, to the blood pigments. The substances are very easily converted into blue, red or green dyes.

3-Acetyl-2 : 4-dimethylpyrrole was condensed with ethyl oxalate in presence of sodium ethoxide, and the product, after evaporating the solvent in vacuum, was acidified with acetic acid, when *ethyl 2 : 4-dimethylpyrryl-3-ethanoneoxalate*, $NH < \begin{matrix} CH=CMe \\ CMe \cdot C \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et \end{matrix}$ was precipitated. The ester crystallises in lemon-yellow leaflets, m. p. 179·5°, forms a *phenylhydrazone*, $C_{18}H_{21}O_5N_3$, pale yellow, slender needles, m. p. 189°, and yields the *hydrazide* of a *ketazine*, $C_{10}H_{13}ON_5$, in thin, glistening, colourless leaflets, m. p. 235°, when mixed with hydrazine hydrate. When left with 2·5% potassium hydroxide, the ester is hydrolysed to 2 : 4-*dimethylpyrryl-3-ethanoneoxalic acid*,

$$C_{10}H_{11}O_4N,$$
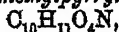
which forms short, golden-yellow, prismatic crystals, decomp. 174°. The ester also dissolves in hot concentrated hydrochloric acid, giving a dark blue solution from which water precipitates the dye in greenish-black masses. On boiling the acid solution for some time, however, the dye separates as an indigo-blue powder. It gives a deep red solution in alkalis.

4-Acetyl-2 : 3-dimethylpyrrole (this vol., i, 196) was also condensed with ethyl oxalate, giving a dark red powder which is insoluble in ether, and also *ethyl 2 : 3-dimethylpyrryl-4-ethanoneoxalate*,

$$NH < \begin{matrix} CMe:CMe \\ CH=C \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et. \end{matrix}$$
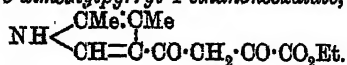
The latter crystallises in long, spindle-like prisms, m. p. 180°, and yields a dark red dye on boiling with concentrated hydrochloric acid.
                                    J. C. W.

Electrolytic Oxidation of Cyclic Ammonium Bases. Otto Fischer and K. Neundlinger (*Ber.*, 1913, **46**, 2544—2546).—The authors required a convenient method of preparation for 1-methyl-2-pyridone from which a ready passage through the corresponding 2-chloro-compound to the 2-amino-compound is available.

The aim is achieved by electrolytic oxidation of 1-methylpyridinium sulphate between iron electrodes with a catholyte and anolyte of sodium hydroxide solution, the latter (D approx. 1·17) containing also some potassium ferricyanide as catalyst (compare Decker and Kaufmann, A., 1911, i, 1023). The yield of 1-methylpyridone (*picrate*, needles, m. p. 145°) is good, both from the point of view of the substance oxidised and the current passed.

By a similar process, 1-methylquinolinium sulphate can be almost quantitatively converted into 1-methyl-2-quinolone.　　D. F. T.

Condensation of Unsaturated Aldehydes with Ammonia and Ethyl Acetoacetate.. II. E. GRISCHKEVITSCH-TROCHIMOVSKI and (Mlle.) I. PAVLOVSKAJA (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 935—946. Compare A., 1911, i, 320).—Ethyl 2 : 6-dimethyl-4-allyldihydropyridine-3 : 5-dicarboxylate, which exhibits the normal molecular weight in freezing benzene or boiling ether, is converted by oxidation with nitrogen trioxide into *ethyl 2 : 6-dimethyl-4-allylpyridine-3 : 5-dicarboxylate*, $C_{16}H_{21}O_4N$, a yellow liquid, b. p. 208·2°/21 mm., $D_4^{16·5}$ 1·0762, $n_D^{16·5}$ 1·5065 ; the corresponding *nitrate*, $C_{16}H_{21}O_4N,HNO_3$, m. p. 85·5°, and the *hydriodide*, $C_{16}H_{21}O_4N,HI$, m. p. 137—140° (decomp.), were prepared (see also *loc. cit.*). The free acid, 2 : 6-*dimethyl-4-allyl-pyridine*-3 : 5-*dicarboxylic acid*, $N{<}{CMe \cdot C(CO_2H) \atop CMe : C(CO_2H)}{>}C \cdot CH : CHMe$, decomposes at about 205° ; its *silver* salt, *hydrochloride*, m. p. about 220° (decomp.), and *platinichloride*, m. p. about 225° (decomp.), were prepared and analysed.

In order to explain the mechanism of the formation of 2 : 4 : 6-trimethylpyridine by the dry distillation of potassium 2 : 6-dimethyl-4-allylpyridine-3 : 5-dicarboxylate (*loc. cit.*), experiments are being made on the condensation of acraldehyde with ethyl acetoacetate and ammonia, which yields ethyl 2 : 6-*dimethyl-4-vinyldihydropyridine-3 : 5-dicarboxylate*, $NH{<}{CMe : C(CO_2Et) \atop CMe : C(CO_2Et)}{>}CH \cdot CH : CH_2$, crystallising in needles, m. p. 86—87°.　　T. H. P.

The Action of 2-Methylindole on Formic Acid. MAX SCHOLTZ (*Ber.*, 1913, **46**, 2539—2542).—Mainly polemical in favour of the views of the author (this vol., i, 895) and König (A., 1911, i, 809) as opposed to those of Ellinger and Flamand (A., 1911, i, 329) concerning the formula of the product of the interaction of 2-methylindole and formic acid.

The *nitrate* of the substance in question has now been prepared in a similar manner to the method recently described (Scholtz, *loc. cit.*) ; it forms ruby-red octahedra, decomp. above 220°, the composition agreeing with the formula $C_{19}H_{16}N_2,HNO_3$, or with the less probable $(C_{28}H_{28}N_3)_2,3HNO_3$.　　D. F. T.

Structure of 3-Nitroso-2-phenylindole. I. and II. LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 150—155, 227—234. Compare Angeli and Morelli, A., 1908, i, 828).—In this preliminary note the author describes some transformations under-

gone by this substance. The production of the *O*-ether described by Angeli and Spica (A., 1899, i, 938) is confirmed. When nitrosophenylindole is heated, small quantities of 2-benzoylaminobenzonitrile are produced. This compound has m. p. 156°, but is readily converted by dilute acids into the corresponding amide, m. p. 216°. The supposed 2-benzoylaminobenzonitrile of Pinnow and Sämann (A., 1896, i, 368) probably consisted of this amide.

By the action of phosphorus pentachloride, 3-nitroso-2-phenylindole is converted into 2-phenyldihydro-4-quinazolone. When 3-nitroso-2-phenylindole is heated with zinc chloride, an apparently isomeric substance, m. p. about 228°, is formed, together with other products. This substance yields the above-mentioned quinazoline derivative when boiled with dilute acids or alkalis, and the same quinazoline derivative is also produced when the amide of m. p. 216° is heated.

The second paper gives experimental details regarding the results recorded in the first paper. 2-Benzoylaminobenzonitrile, prepared either by heating nitrosophenylindole (*loc. cit.*), or from 2-aminobenzonitrile, crystallises in colourless prisms or in long needles, m. p. 156°.   R. V. S.

Scission of Decahydroquinoline into the Two Optical Antipodes. BRUNO VENEZIANI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 155—157).—Synthetical decahydroquinoline can be resolved with the aid of *d*-bromocamphorsulphonic acid. d-*Decahydroquinoline* d-*bromocamphorsulphonate* forms acicular crystals, m. p. about 220°, $[a]_D^{27}$ +64·01° (in 1·117% aqueous solution), and is less soluble than the *l*-salt, which was obtained only in the form of an oil. d-*Decahydroquinoline* has $[a]_D^{27}$ +1·28° (in 4·013% ethereal solution). l-*Decahydroquinoline* has $[a]_D^{27}$ −1·02° (in 14·11% ethereal solution). In consequence of the small quantity of substance available, the author suggests that the rotatory powers of the pure enantiomorphs may be numerically greater than those above recorded.   R. V. S.

Arsenic Compounds of the Quinoline Group. SIGMUND FRÄNKEL and PAUL LÖWY (*Ber.*, 1913, 46, 2546—2550).—The authors have turned their attention to the arsenic compounds of quinoline because both constituents of such molecules would be physiologically active.

Schiff (*Annalen*, 1864, 131, 116) has already given a brief report on certain compounds from quinoline and arsenic trichloride. It is now found that the action of quinoline and analogous bases with arsenic trichloride is an additive one ; the action was effected in ethyl acetate solution with equimolecular quantities of the reagents. *Quinoline arsenotrichloride*, $C_9H_7N,AsCl_3$, is a colourless solid, m. p. 138° ; *tetrahydroquinoline arsenotrichloride*, $C_9H_{11}N,AsCl_3$, is a pink solid, m. p. 134° ; *8-hydroxyquinoline arsenotrichloride*, $C_9H_7ON,AsCl_3$, is a bright yellow substance, m. p. 168°. Even under the influence of aluminium chloride the arsenic atom could not be made to enter the quinoline nucleus, and a similar failure was experienced when quinoline and tetrahydroquinoline were heated with arsenic acid at 200° in a sealed

tube, the products being *quinoline arsenate*, bright yellow leaflets, decomp. at 250°, and *tetrahydroquinoline arsenate*, colourless leaflets, m. p. 123°.

Attempts to synthesise the quinoline nucleus from arsanilic acid by Skraup's method gave merely quinoline, whilst Knorr's process with ethyl acetoacetate left the arsanilic acid unaltered. However, arsanilic acid condenses with acetaldehyde when an intimate mixture is treated with hydrobromic acid (D 1·49) ; the *hydrochloride* of 2-*methylquinoline-arsinic acid*, a yellow, crystalline solid, separates, from which the free acid, decomp. at 140°, can be liberated by washing with distilled water. Reduction of this acid in alcohol by sodium yields the tervalent arsenic compound, 2-*methylquinolinearsenoxide*, decomp. at 120°; the *picrate* was prepared.   D. F. T.

Synthesis of 2-Cyanoquinoline and 1-Cyanoisoquinoline. ADOLF KAUFMANN and PAUL DÄNDLIKER (*Ber.*, 1913, **46**, 2924—2929). —2-Cyanoquinoline, already prepared by Pfitzinger (Abstr., 1902, i, 53), was made by treating Reissert's 2-cyano-1-benzoyl-1 : 2-dihydro-quinoline, dissolved in chloroform, with phosphorus pentachloride. It is readily hydrolysed to quinaldinic acid, which is also formed as a by-product in the preparation of the cyano-base.

1-*Cyanoisoquinoline*, similarly obtained from 1-cyano-2-benzoyl-1 : 2-dihydroisoquinoline (Reissert, Abstr., 1905, i, 926) has m. p. 74°, crystallises from light petroleum, and is very soluble in ether or alcohol, but sparingly in water. On hydrolysis by acids or alkalis, it yields *iso*quinaldinic acid (*iso*quinoline-1-carboxylic acid).   T. A. H.

Preparation of Arylquinolinecarboxylic Acid Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 261028).— *Salicyl 2-phenylquinoline-4-carboxylate*, colourless leaflets, m. p. 188°, is obtained when a benzene solution of 2-phenylquinoline-4-carboxylic acid is warmed during two hours with thionyl chloride and the solid residue (left after evaporating the solvent) mixed with salicylic acid and benzene and heated during three hours at 80°.

o-*Hydroxytoluoyl* 2 : 3-*diphenylquinoline-4-carboxylate*, colourless needles, m. p. 250°, is prepared in an analogous manner from hydroxy-toluic acid and 2 : 3-diphenylquinoline-4-carboxylic acid. *Salicyl* 2-p-*anisylquinoline-4-carboxylate*, colourless needles, has m. p. 132°, and *salicylglycine 2-phenylquinolinecarboxylate*, m. p. 120°.   F. M. G. M.

Quinolyl Ketones. III. ADOLF KAUFMANN, PAUL DÄNDLIKER and HANS BURKHARDT (*Ber.*, 1913, **46**, 2929—2935. Compare Abstr., 1912, i, 1017 ; this vol., i, 294).—It is now shown that in the pre-paration of these ketones by the use of Grignard reagents with cyanoquinolines, a molecule of the magnesium alkyl iodide is first attached to the cyclic nitrogen and then a second molecule to the cyano-group. The position of the cyano-group has some influence on the reactions; thus 2-cyanoquinoline and 1-cyanoisoquinoline give good yields of the corresponding alkyl ketones, whilst 5-cyanoquinoline does not react with Grignard reagents.

2-*Quinolyl methyl ketone*, $C_9H_6N \cdot COMe$, m. p. 52°, b. p. 146—148°/

13 mm., forms small needles from dilute alcohol, and has a jasmine-like odour. The *phenylhydrazone*, m. p. 154°, crystallises from alcohol in slender, yellow needles. 2-*Quinolyl ethyl ketone*, m. p. 59—60°, distils in steam, forms colourless needles from alcohol, and has a pleasant ketone-like odour. The *phenylhydrazone*, m. p. 106°, forms short, yellow needles. 2-Quinolyl phenyl ketone was also prepared by this means (compare Besthorn, 1908, i, 681). 2-*Quinolyl benzyl ketone*, m. p. 78°, crystallising in flat needles, was prepared by treating 2-cyanoquinoline with magnesium methyl iodide followed by magnesium benzyl chloride, or by the action of ethyl quinaldinate on the sodium derivative of benzyl cyanide, which gave 2-*quinolyl cyanobenzyl ketone*, m. p. 120—121°, long needles, which was then hydrolysed to the corresponding *acid* and the latter heated at 120—130°.

1-iso*Quinolyl methyl ketone*, m. p. 48°, crystallises in colourless needles, is readily soluble in organic solvents, and has only a slight odour. The *phenylhydrazone* decomposes at 160°. 1-iso*Quinolylphenyl ketone*, m. p. 76—77°, b. p. 231°/12 mm., crystallises in highly refractive tablets, is readily soluble in benzene, alcohol or ether, but sparingly in light petroleum. It does not yield a methiodide with methyl iodide at 100° under pressure. T. A. H.

New Synthesis of Carbostyril. HANS MEYER and ROBERT BEER (*Monatsh.*, 1913, **34**, 1173—1179).—When o-chlorocinnamic acid is heated with copper and ammonia solution it is partly converted into carbostyril (2-hydroxyquinoline), the reaction being almost complete when the mixture is heated during thirty hours at 160—170°. At 120—130°, on the contrary, more or less o-aminocinnamic acid is also formed. A process for the isolation of the latter is described. The o-aminocinnamic acid produced in this reaction differs in certain respects from that prepared by reduction of o-nitrocinnamic acid, being (1) more soluble in water ; (2) not readily convertible into coumarin, and (3) of different melting point, namely, 150°. It seems possible that it may be a new *trans*-form of the acid (compare Stoermer and Heymann, Abstr., 1912, i, 974).

When 2-methoxyquinoline is (1) distilled under atmospheric pressure, (2) heated on a water-bath, or (3) kept for some time in diffused light, it passes into the non-volatile isomeride in which the methyl group is attached to the nitrogen, a change analogous with the conversion of a-methoxypyridine into *N*-methylpyridine (compare Abstr., 1901, i, 343).

o-Chlorophenylpropionic acid when heated at 140—160° with copper and ammonia solution during thirty hours is converted quantitatively into hydrocarbostyril. T. A. H.

Nitro-derivatives of Thiodiphenylamine [Phenthiazine]. FRIEDRICH KEHRMANN and OLGA NOSSENKO (*Ber.*, 1913, **46**, 2809—2820).—The nitrophenthiazinesulphoxides obtained by the action of nitric acid on phenthiazine (Bernthsen, A., 1886, 53) are converted into the corresponding nitrophenthiazines by mineral acids in the presence of alcohol or glacial acetic acid ; the most suitable reagent is concentrated hydrochloric and glacial acetic

acids, although it has a tendency to replace nitro-groups by chlorine atoms and to form chlorinated products. Smiles and Barnett (T., 1909, **95**, 1261) and Claasz (A., 1912, i, 513) have examined the action of such reagents on nitrated phenthiazinesulphoxides and have described the products as derivatives of phenazothionium hydroxide. This is incorrect, the products obtained by these investigators being nitrophenthiazines mixed with chlorinated and oxidised by-products.

5-Nitrophenthiazine, $C_6H_4\underset{S}{\overset{NH}{\diagup\diagdown}}C_6H_3 \cdot NO_2$, m. p. 111°, violet-black leaflets, is obtained by condensing *o*-aminophenyl disulphide with 1-chloro-2 : 6-dinitrobenzene (2 mols.) in boiling alcohol in the presence of sodium acetate (2 mols.), and reducing the resulting dinitrodiphenylamine disulphide in boiling alcohol and benzene with concentrated aqueous sodium sulphide; the yield is very unsatisfactory. By reduction with stannous chloride and hydrochloric acid, it is converted into *5-aminophenthiazine hydrochloride,* colourless needles, which is oxidised by aqueous ferric chloride to *5-aminophenazothionium chloride,* $C_6H_4\underset{SCl}{\overset{N}{\diagup\diagdown}}C_6H_3 \cdot NH_2$, which is isolated as the *platini-chloride,* $2C_{12}H_9N_2SPtCl_6$, greyish-green crystals. 5-Aminophenthiazine forms an *acetyl* derivative, m. p. 174°, colourless prisms.

3-Nitrophenthiazine, m. p. 218°, violet-black crystals, is obtained by treating an alcoholic suspension of 3-nitrophenthiazinesulphoxide with 30% sulphuric acid, warming finally on the water-bath. The sulphoxide is converted by hydrochloric and acetic acids into *9(?)-chloro-3-nitrophenthiazine,* $C_6H_3Cl\underset{S}{\overset{NH}{\diagup\diagdown}}C_6H_3 \cdot NO_2$, m. p. about 268°, brownish-black, bronze needles; by reduction, the latter yields the chloroaminophenthiazine by the oxidation of which by ferric chloride the chloroaminophenazothionium chloride is obtained.

The action of hydrochloric and acetic acids on 3 : 9-dinitrophenthiazinesulphoxide yields a mixture of 3 : 9-dinitrothiodiphenylamine and a *tetrachloro*-derivative, m. p. 235°, colourless needles (probably *3 : 5 : 7 : 9-tetrachlorophenthiazine*), which is separated by extracting the latter with chloroform. *3 : 9-Dinitrophenthiazine,*

$$NO_2 \cdot C_6H_3\underset{S}{\overset{NH}{\diagup\diagdown}}C_6H_3 \cdot NO_2,$$
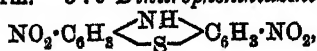
m. p. 276°, dark brownish-red needles, forms solutions with a characteristic brick-red fluorescence and yields by reduction the leuco-derivative of Lauth's violet. It is also the chief product of the action of solid sodium nitrite on a suspension of phenthiazine in glacial acetic acid.

Smiles and Barnett's tetranitrophenthiazinesulphoxide (*loc. cit.*) is, contrary to their statement, practically unchanged by treatment with alcohol and mineral acids. From the by-products in its preparation a *substance,* $C_{12}H_6O_8N_4S$, m. p. 270°, yellow needles, is obtained, which is probably a *hydroxytrinitrophenthiazinesulphoxide.*

Attention is called to the fact that all nitrophenthiazines containing at least one nitro-group in the para-position to the nuclear nitrogen

atom form intensely blue or green alkali salts, which probably have the quinonoid constitution $C_6H_4\!\!<^N_S\!\!>C_6H_3{:}NO{\cdot}OM$.   C. S.

Preparation of Anthraquinonedithiazoles and their Reduced Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 260905).— 2 : 6-*Diaminoanthraquinone*-1 : 5-*dimercaptol* is obtained by heating 1 : 5-dichloro-2 : 6-diaminoanthraquinone with an aqueous-alcoholic solution of sodium polysulphide under pressure, and it has been employed in the preparation of the following *compounds* : (1) by boiling the foregoing mercaptol (50 parts) with 50 to 100 parts of either benzaldehyde, benzylidene chloride, benzotrichloride, or benzoyl chloride ; (2) in a similar manner with *p*-dimethylaminobenzaldehyde ; (3) with anthraquinone-2-aldehyde.

The tinctorial properties of these compounds are described, also modifications in methods of preparation, whilst the same reaction with other aldehydes and mercaptols is also discussed.   F. M. G. M.

Quinone-benzidine and its Reaction Products. KURT BRASS (*Ber.*, 1913, **46**, 2902—2906).—When the components are brought together in toluene, 2 mols. of benzidine unite with 1 mol. of quinone to form a soluble bluish-black addition product (compare Fecht, A., 1908, ii, 916). On warming in alcohol, an insoluble brown powder is obtained containing benzidine and quinone in molecular proportions.

The bluish-black product crystallises in platelets, m. p. 118°. The brown product does not melt ; it dissolves with a blue coloration in concentrated sulphuric acid, and probably represents a polymeride.

Chloranil and benzidine when warmed together in toluene solution condense to an insoluble brown vat dye, which is regarded as a mixture of dibenzidinodichloroquinone with a little monobenzidinotrichloroquinone.   E. F. A.

Oxidation of Anilinoquinones to Benzidine Derivatives. II. KURT BRASS (*Ber.*, 1913, **46**, 2907—2912. Compare A., 1912, i, 874).—1-Anilinoanthraquinone is readily oxidised by manganese dioxide and sulphuric acid to N : N'-bis*anthraquinonyl-1-benzidine*, a clear violet vat dye, which is composed of microscopic, transparent, violet crystals, m. p. 311°. The solution in concentrated sulphuric acid is olive-green.

In a similar manner, 1-anthra-anilinoanthraquinone may be oxidised to N : N'-*bis-(anthraquinonyl-1)-benzidine*-o-*dicarboxylic acid*, which forms a mass of violet-red needles, m. p. about 360°. On heating in concentrated sulphuric acid at 100—110°, the green solution becomes orange, and *dianthraquinone-2 : 1-acridone*,

$$C_6H_4\!\!<^{CO}_{CO}\!\!>C_6H_2\!\!<^{CO}_{NH}\!\!>C_6H_3{\cdot}C_6H_3\!\!<^{CO}_{NH}\!\!>C_6H_2\!\!<^{CO}_{CO}\!\!>C_6H_4$$
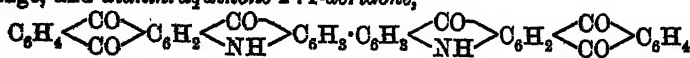
is obtained in the form of a mass of pale violet needles. It does not melt or sublime.

Bis-a-naphthoquinonyl-2-benzidine, obtained on oxidation of anilino-*a*-naphthoquinone, gives a brownish-violet solution in concentrated sulphuric acid.   E. F. A.

Phenylhydrazine. I. Anhydrous Phenylhydrazine as a Cryoscopic Solvent. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 263—274).—The cryoscopic constant of phenylhydrazine is 58·59 (from experiments with naphthalene, diphenyl, dibenzyl, veratrole, and safrole). The molecular weight of hydrocarbons (benzene, toluene, *p*-xylene, and *p*-cymene) dissolved in phenylhydrazine increases with the concentration, and the same phenomenon is observed with alcohols (ethyl alcohol, *iso*butyl alcohol, *iso*amyl alcohol, and ethylene glycol); triphenylcarbinol gives a value below the normal at all concentrations. Phenols (phenol, *p*-cresol, and β-naphthol) have molecular weights below the theoretical value, and they diminish slowly when the concentration is increased. Bases (pyridine, piperidine, aniline, dimethylaniline, and quinoline) behave normally. Acetic acid and butyric acid are almost normal, whilst benzoic acid and salicylic acid have molecular weights much below the calculated values. R. V. S.

Phenylhydrazine. II. The System Phenylhydrazine–Water and the Cryoscopic Constant of Hydrated Phenylhydrazine. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 274—281. Compare preceding abstract).—Phenylhydrazine and phenylhydrazine hydrate show an eutectic point at 16°, and there is a maximum corresponding with the formula $(NHPh\cdot NH_2)_2,H_2O$, which agrees with that of the phenylhydrazine hydrate already known. The cryoscopic constant of phenylhydrazine hydrate is 44·15 (from experiments with diphenyl, veratrole, and naphthalene). R. V. S.

Phenylhydrazine. III. Velocity of Reaction of Aldehydes and Ketones with Phenylhydrazine. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 354—362. Compare preceding abstracts).—Comparative cryoscopic experiments show that the reaction of phenylhydrazine with acetone is complete in forty minutes, that with acetophenone in 162 minutes, whilst that with benzophenone has hardly begun after 225 minutes. Tables are also given showing the cryoscopic behaviour of a number of aldehydes and ketones in phenylhydrazine. R. V. S.

Action of Stannic Chloride on Phenylhydrazine. JITENDRA N. RAKSHIT (*J. Proc. Asiatic Soc., Bengal*, 1913, **9**, 131—135, Reprint).—Pure stannic chloride reacts very vigorously with phenylhydrazine, yielding benzene and nitrogen, whilst phenylhydrazine hydrochloride may be isolated from the product by dissolving it in water, precipitating the tin as the sulphide, and concentrating. A quantitative study of the reaction has shown that two molecules of the base give rise to one molecule of benzene, one of phenylhydrazine hydrochloride, and one of nitrogen. The equation:

$$2NHPh\cdot NH_2 + SnCl_4 = C_6H_6 + N_2 + SnCl_2 + NHPh\cdot NH_2,2HCl$$
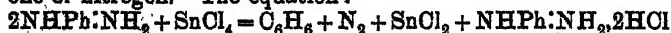
agrees with these results, but introduces the anomaly that phenylhydrazine forms a dihydrochloride. Such an easily decomposable compound would be analogous to the dihydrofluoride described by Thieme (A., 1893, i, 155), and since no double salt of the base with a chloride of tin could be detected, its existence must be taken for granted.

The question whether the benzene is formed through the intervention of benzenediazonium chloride remains to be proved.

<div align="right">J. C. W.</div>

Mutual Replacement of Ammonia and Amines in Carbon Compounds. N. CONEV and PAVEL IV. PETRENKO-KRITTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1092—1098).—In order to throw light on the results obtained by Schöttle and Petrenko-Krittschenko (A., 1911, i, 1020 ; 1912, i, 128 ; this vol., i, 48), the authors have investigated the action of ammonia and amines on acetylphenylmethyl-pyridonone (compare von Pechmann and Neger, A., 1893, i, 398), which differs from benzoyldehydracetic acid in that the two phenyl side-groups are replaced by methyl groups. The substituents have such a considerable influence on the course of the reaction that the latter is of an entirely different character from that previously observed. The ring is here found to exhibit great stability, substitution of oxygen and mutual replacement of ammonia and amines taking place only in the side-chains. Further, heating of acetylphenylmethylpyridonone with hydrochloric acid results in the separation, not of aniline, but of acetic acid.

The action of ammonia on 5-acetyl-1-phenyl-2-methylpyridonone gives a quantitative yield of the *compound,*

$$CMe{<}{CH-CO \atop NPh\cdot CO}{>}C{:}CMe\cdot NH_2,$$
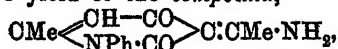
m. p. 247—248°. Similarly, the action of methylamine gives the *compound,* $CMe{<}{CH-CO \atop NPh\cdot CO}{>}C{:}CMe\cdot NHMe$, in colourless, thin needles, m. p. 183°, and that of aniline the *compound,* $C_{19}H_2O_2N{:}CMe\cdot NHPh$, m. p. 154—155°.

When these derivatives are subjected to suitable conditions, the methylamine or aniline residue may be replaced by the amino-group, the latter by the methylamine or aniline residue, or the aniline by the methylamine group.

1-*Phenyl-2-methylpyridonone,* $NPh{<}{CMe{:}CH \atop CO-CH_2}{>}CO$, obtained by heating the acetyl compound with excess of concentrated hydrochloric acid in a sealed tube at 150°, forms transparent, lustrous plates, m. p. 270—271°, and yields an *acetyl* derivative, $NPh{<}{CMe{:}CH \atop CO-CH}{>}C\cdot OAc$, which crystallises in needles, m. p. 146—147°, and is isomeric with von Pechmann and Neger's compound (*vide supra*). With benzaldehyde, it yields 1-*phenyl-5-benzylidene-2-methylpyridonone,*

$$NPh{<}{CMe{=\!=\!=}CH \atop CO\cdot C({:}CHPh)}{>}CO,$$
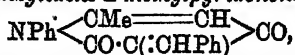
m. p. 308—309°, which has the normal molecular weight in freezing phenol.

<div align="right">T. H. P.</div>

Synthesis of Aminoacetyl - 8 - methoxyquinoline. SIGMUND FRÄNKEL and OSKAR GRAUER (*Ber.*, 1913, **46**, 2551—2554).—After several fruitless attempts to prepare substances which should constitu-

tionally resemble adrenaline, the authors have obtained the above substance.

8-Methoxyquinoline was prepared by the method of Bedall and Fischer (A., 1882, 412) improved by the replacement of ether by benzene for the purpose of extraction ; the base, needles, b. p. 172°/24 mm., gives a *platinichloride*, and a *picrate*, decomp. at 143°. When treated in light petroleum with chloroacetyl chloride and aluminium chloride, the methoxyquinoline is slowly converted into *chloroacetyl-8-methoxyquinoline*, a volatile, colourless solid, m. p. 58°, b. p. 152°/22 mm., which powerfully attacks the skin and eyes. Although the action of ammonia on this substance caused resinification, a mixture with potassium phthalimide in a sealed tube at 160—170° gave rise to *phthaliminoacetyl-8-methoxyquinoline*, a colourless solid, m. p. 219°, which by hydrolysis with concentrated hydrochloric acid in a sealed tube was converted into *aminoacetyl-8-methoxyquinoline hydrochloride*, $OMe \cdot C_9H_5N \cdot CO \cdot CH_2 \cdot NH_2, 1\frac{1}{2}HCl$, m. p. 198° (decomp.). D. F. T.

Reactivity of the Methyl Group in 3-Amino-2-methylquinoline. OTTO STARK and FELIX HOFFMANN (*Ber.*, 1913, **46**, 2697—2703). —Unsuccessful attempts have been made to involve the methyl group of 2-methyl-3-aminoquinoline in condensations with formaldehyde or carbonyl chloride. Further, ring formation is not observed when 3-amino-2-methylquinoline is diazotised, nor could it be brought about by the elimination of water from 3-acetylamino-2-methylquinoline, although, in the latter case, the basicity of the amino-group is weakened by introduction of the acetyl radicle.

When a solution of 3-amino-2-methylquinoline in hydrochloric acid is warmed with formaldehyde, a salt separates from which sodium hydroxide liberates the *base* (annexed formula), m. p. 204—205°. The *hydrochloride*, yellow, prismatic needles, m. p. 210—211°, and the *platinichloride*, yellow needles, m. p. 234—235°, were analysed. Boiling aqueous hydrochloric acid slowly decomposes the base into aminoquinaldine and formaldehyde.

Di-2-methylquinolinecarbamide, $C_{21}H_{18}ON_4$, m. p. 278°, is obtained when a solution of 3-amino-2-methylquinoline in dry toluene is left in contact with a solution of carbonyl chloride in the same solvent during two days and the product decomposed with $2N$-sodium hydroxide. The *hydrochloride*, $C_{21}H_{18}ON_4, 2HCl$, pale yellow needles, has m. p. 232—233°.

When a diazotised solution of 3-amino-2-methylquinoline is neutralised with sodium hydrogen carbonate and the precipitate dissolved in ether, a red, crystalline *powder* is obtained (after removal of the solvent), which has m. p. 105—115°, from which a definite substance could not be isolated. A solution of aniline hydrochloride, however, yields *2-methylquinolinediazoaminobenzene*, yellow crystals, m. p. 158°, when added to a diazotised solution of 3-amino-2-methylquinoline hydrochloride in the presence of sodium acetate. The corresponding *aminoazo*-compound, reddish-yellow crystals, m. p. 98—99°, is readily obtained by the usual methods. H. W.

Constitution of the Blood and Bile Pigments. II. HANS
FISCHER and ERICH BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1913, **87**,
255—269. Compare this vol., i, 209).—Further examples of the
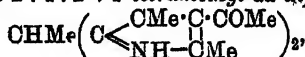coupling of pyrrole nuclei in the 2-position to a carbon atom are
described.

Equimolecular quantities of ethyl 2 : 5-dimethylpyrrole-3-carboxylate
and ethyl 2 : 4-dimethylpyrrole-3-carboxylate couple with formaldehyde
to form *ethyl 2 : 5 : 2′ : 4′-tetramethyldipyrrylmethane-3′ : 4-dicarboxylate*,

$$\begin{matrix} C Me{:}C(CO_2Et) \\ NH{-}\!\!-\!\!-CMe \end{matrix} {>} C{\cdot}CH_2{\cdot}C {<} \begin{matrix} NH{-}CMe \\ CMe{\cdot}C{\cdot}CO_2Et{\cdot} \end{matrix}$$

This forms faintly yellow
crystals, m. p. 178—179°. From acetone, it crystallises in long,
colourless needles.

Ethyl   2 : 5′ : 2′ : 5-tetramethyldipyrrylmethane-3 : 3′-dicarboxylate,
formed in a similar manner, separates as a colourless, crystalline
powder, m. p. 231—232°, after previously sintering.

Ethyl   5-acetyl-2 : 4 : 2′ : 4′-tetramethyldipyrrylmethane-3′-carboxylate
crystallises in colourless needles in fan-like aggregates, m. p. 188—189°.

Ethyl   3-acetyl-2 : 4 : 2′ : 4′-tetramethyldipyrrylmethane-3′-carboxylate,
crystallises in yellow prisms belonging to the rhombic system,
m. p. 231—232°.

Ethyl 3 : 3′-diacetyl-2 : 4 : 2′ : 4′-tetramethyl-αα-dipyrrylethane,

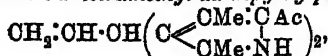$$CHMe \left(C {<} \begin{matrix} CMe{\cdot}C{\cdot}COMe \\ NH{-}CMe \end{matrix} \right)_2,$$

obtained on condensing acetyldimethylpyrrole with acetaldehyde,
crystallises in colourless, rectangular platelets, m. p. 251—252°.

Ethyl   2 : 4 : 2′ : 4′-tetramethyl-αα-dipyrrylethane-3 : 3′-dicarboxylate
separates in well formed, colourless crystals, m. p. 171—172°.

Ethyl 3-acetyl 2 : 4 : 2′ : 4′-tetramethyl-αα-dipyrrylethane-3′-carboxylate,
crystallises in hexagonal tablets; m. p. 202—203°, but giving a clear
flux only at 209°.

5 : 5′-Diacetyl-2 : 4 : 2′ : 4′-tetramethyl-αα-dipyrrylpropylene,

$$CH_3{:}CH{\cdot}OH \left(C {<} \begin{matrix} CMe{:}C Ac \\ CMe{\cdot}NH \end{matrix} \right)_2,$$

formed on condensing acetyldimethylpyrrole with an alcoholic solution
of acraldehyde, was obtained as a yellow, microcrystalline powder.

5-Bromo-3-acetyl-2 : 4-dimethylpyrrole, $NH {<} \begin{matrix} CMe{:}CAc \\ CBr{\cdot}CMe \end{matrix}$, obtained on

brominating acetyldimethylpyrrole in acetic acid, crystallises in faintly
yellow prisms, m. p. 165—166° (decomp.).

Pyrroles couple with diazo-compounds more easily in the 2- than in
the 3-position. Accordingly, in a mixture of 2 : 4-dimethylpyrrole and
2 : 4-dimethyl-5-ethylpyrrole on the cautious addition of diazobenzene-
sulphonic acid the former is completely precipitated. On adding more
of the diazo-compound to the filtrate, the latter (3-position free) is also
completely precipitated as azo-dye.   E. F. A.

New Class of Quinoline Dyes. III. EMIL BESTHORN (*Ber.*,
1913, **46**, 2762—2770).—The dye, $C_{19}H_{12}ON_2$, obtained by the methods

previously described (Besthorn and Ibele, A., 1904, i, 527; 1905, i, 612), probably has the annexed con- constitution; it is certainly not 2 : 2'-di- quinolyl ketone (Gebhard, A., 1909, ii, 284), since its properties are quite different from those of 2-quinolyl phenyl ketone (A., 1908, i, 681).
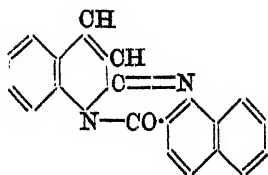
The asymmetric structure of the dye is proved as follows. If the dye is 2 : 2'-di- quinolyl ketone, it is evident that the sub- stances produced from quinaldinyl chloride and 4-phenylquinoline and from 4-phenylquinaldinyl chloride and quinoline must in each case be be 4-phenyl-2 : 2'-diquinolyl ketone. Actually, the two products are different. 4-*Phenylquinaldinyl chloride*, m. p. 116°, and quinoline in benzene at the ordinary temperature yield a *substance*, $C_{25}H_{16}ON_2$, m. p. above 240°, brownish-red crystals, which is converted into carbostyril and 4-phenylquinaldinic acid by concentrated sulphuric acid at 70—75°. The *substance*, $C_{25}H_{16}ON_2$, produced from quin- aldinyl chloride and 4-phenylquinoline has m. p. above 240°, forms brownish-red crystals, and yields quinaldinic acid and 4-phenylcarbo- styril by treatment with concentrated sulphuric acid at 70°.

In a similar manner, quinaldinyl chloride and ethyl cinchoninate in benzene yield a *substance*, $\begin{matrix} C_6H_4\text{---}N\text{===}C\text{---}CH \\ CH:CH\cdot C\cdot CO\cdot N\cdot C_6H_4 \end{matrix}>C\cdot CO_2Et$, m. p. 238°, brownish-red needles with a green reflex, which resembles other dyes of the same type in forming strongly fluorescent solutions.

These quinoline dyes are more sensitive to sunlight than any other class of organic dyes; a change, however, only occurs in the presence of oxygen. Under such conditions in benzene, the preceding dye is rapidly decolorised, ethyl 2-hydroxycinchoninate being formed, whilst the dye from quinaldinyl chloride and 4-phenylquinoline yields 4-phenylcarbostyril; products corresponding with the other halves of the two molecules cannot be isolated. C. S.

Hydantoins. XXV. The Preparation of Hydantoin from Hippuric Acid. TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1913, 35, 1605—1606).—When a specimen of hydantoin is required urgently and potassium cyanate is not available, the following method is convenient.

Hippuric acid (or, indeed, any α-acylamino-acid) is first converted into 3-benzoyl-2-thiohydantoin, which is possible with excellent yields (Johnson and Nicolet, A., 1912, i, 53). This substance is then desulphurised by digesting with an aqueous solution of chloroacetic acid when hydrolysis concurrently occurs, the products therefore being benzoic acid and hydantoin. D. F. T.

Hydantoins. XXVI. Syntheses of 4-Hydroxy-3-methoxy- phenylalanine and 3 : 4-Dimethoxyphenylalanine. TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1913, 35, 1606—1617).—Vanillin condenses with hydantoin when heated

together with anhydrous sodium acetate in acetic acid, the product being 4-p-*hydroxy-m-methoxybenzylidenehydantoin*,

$$\begin{matrix} NH-CO \\ CO\cdot NH \end{matrix}\Big> C\colon CH\cdot C_6H_3(OMe)\cdot OH,$$
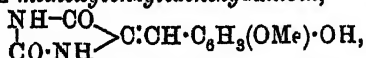
a granular solid, m. p. 264—265°; this was reduced by tin and an alcoholic solution of hydrogen chloride with formation of 4-p *hydroxy-m-methoxybenzylhydantoin*, prisms, m. p. 194—195°.

The condensation product of vanillin with 2-thiohydantoin, obtainable under similar conditions to the above, was 2-*thio-4-p-hydroxy-m-methoxybenzylidenehydantoin*, yellow needles, m. p. 232—233°, which gives a blood-red solution in concentrated sulphuric acid and a yellow one in aqueous sodium hydroxide solution. When digested with an aqueous solution of chloroacetic acid, it undergoes desulphurisation to the above 4-p-hydroxy-m-methoxybenzylidenehydantoin, and on reduction in aqueous suspension by sodium amalgam becomes converted into 4-*hydroxy-3-methoxybenzylthiohydantoic acid*,

$$OH\cdot C_6H_3(OMe)\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CS\cdot NH_2,$$
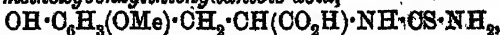
yellow prisms from aqueous solution, m. p. 181—182° (decomp.). Reduction of the thiomethoxyhydroxybenzylidenehydantoin by tin or by stannous chloride in each case with an alcoholic solution of hydrogen chloride gave the 4-p-hydroxy-m-methoxybenzylhydantoin described above. The last-named substance when submitted to the action of boiling barium hydroxide solution for many hours evolves ammonia and 4-*hydroxy-3-methoxyphenylalanine*,

$$OH\cdot C_6H_3(OMe)\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$
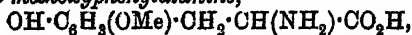
prisms (with $1H_2O$), m. p. 255—256° (decomp.), is simultaneously produced.

Veratraldehyde condenses with 2-thiohydantoin, under the conditions described above, with formation of 2-*thio-4-mp-dimethoxybenzylidenehydantoin*, prisms, m. p. 229—230°, which can be reduced in suspension in water by sodium amalgam to 2-*thio-4-mp-dimethoxybenzylhydantoin*, crystals with $1H_2O$, m. p. 102—103°. When desulphurised by aqueous chloroacetic acid, this gives rise to 4-mp-*dimethoxybenzylhydantoin*, a viscous syrup, from which 3 : 4-*dimethoxyphenylalanine*, hair-like crystals, m. p. 249—250° (decomp.), can be obtained by digestion with barium hydroxide solution.

When 4-p-hydroxy-m-methoxybenzylidenehydantoin is treated with alcoholic potassium hydroxide and methyl iodide, methylation occurs with production of 1-*methyl-4-mp-dimethoxybenzylidenehydantoin*, prismatic crystals, m. p. 218°, together with some 1 : 3-*dimethyl-4-mp-dimethoxybenzylidenehydantoin*, distorted prisms, m. p. 122—124°, which gives a bright red solution in sulphuric acid.   D. F. T.

β-**Naphthalaninehydantoic Acid.** WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, **55**, 477—480).—Kikkoji (Abstr., 1911, ii, 909) has obtained from the urine, after administration of β-naphthalanine to a dog, a substance to which the formula $C_{15}H_{16}O_3N_2$ was assigned. As it is known that amino-acids on evaporation in urine react with the urea to yield uraminic acids, it is conceivable that the above-mentioned substance is a derivative of this character formed from unchanged β-naphthalanine. By the action of urea on β-naphthalanine in the

presence of barium hydroxide, a β-naphthalaninehydantoic acid, $C_{14}H_{14}O_8N$, could be obtained with m. p. 194—195°. Kikkoji's substance melted at 190°, so that the identity of the two products cannot yet be regarded as proved, especially as Kikkoji's analyses are not in strict accordance with those of the synthetic substance.

<div style="text-align:right">S. B. S.</div>

Preparation of a Mercury Derivative of the Pyrazolone Series. LEON GIVAUDAN and EMIL SCHEITLIN (D.R.-P. 261081 and 261082).—When 300 parts of 4-sulphamo-1-phenyl-2 : 3-di-methyl-5-pyrazolone (A., 1908, i, 688) are gently warmed with freshly prepared mercuric oxide (from 270 parts of mercuric chloride) in 10,000 parts of water, it furnishes a colourless, crystalline *compound*, I or II (the latter being considered most probable) ; it contains

OMe   OMe

NMe⟨ ⟩C·NH·SO₃Hg   NMe⟨ ⟩C·N(SO₃H)·HgOH
NPh⌐—⌐CO   NPh⌐—⌐CO
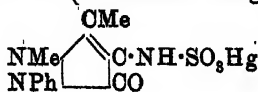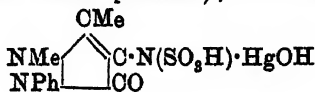
(I.)   (II.)

41% of mercury, and, when treated with dilute alkalis, part of the mercury separates in the mercurous condition, leaving a compound in solution containing 24% of mercury.

II. States that by altering the proportions of reacting material in the foregoing preparation, a *compound*, a greenish-white powder containing 67—68% Hg, is obtained, by treatment with sodium hydroxide part of the mercury is eliminated, and the solution furnishes the previously described compound containing 24% of mercury.

<div style="text-align:right">F. M. G. M.</div>

Antipyrine and Ammonia Compounds of Some Nitrates of the Rare Earths. ADALBERT KOLB (*Zeitsch. anorg. Chem.*, 1913, **83**, 143—148. Compare A., 1909, i, 16).—*Zirconium nitrate antipyrine*, $Zr(NO_3)_4,6C_{11}H_{12}ON_2$, prepared in nitric acid solution, forms colourless tablets, m. p. 217—218° (decomp.), readily soluble in water. *Thorium nitrate antipyrine*, $2Th(NO_3)_4,5C_{11}H_{12}ON_2$, readily forms supersaturated solutions and has m. p. 168—169°. The *lanthanum, cerous*, and *samarium* compounds contain 3 mols. of antipyrine, and have m. p.'s 161—162°, 165°, and ¦177—178° respectively. *Erbium nitrate antipyrine*, $Er(NO_3)_3,4C_{11}H_{12}ON_2$, forms pink tablets, and has m. p. 175—176°, whilst the *yttrium* compound is colourless and has m. p. 176—177°.

Thorium nitrate combines with ammonia, forming compounds, $Th(NO_3)_4,2H_2O,3NH_3$ and $2Th(NO_3)_4,3H_2O,7NH_3$. An anhydrous salt, formed with the development of much heat, proves to be basic, $ThNO_3(OH)_3$. Zirconium also forms a crystalline basic compound, $ZrO(NO_3)_2,2H_2O,2NH_3$.

<div style="text-align:right">C. H. D.</div>

Benzylated Pyrazole Derivatives and a Peculiar Case of Autoalkylation. PAUL JACOBSON and H. JOST (*Annalen*, 1913, **400**, 195—219).—By boiling with about 16% alcoholic potassium hydroxide for one hour, 1-phenyl-2-benzyl-3-methyl-5-pyrazolone decomposes and yields ammonia, 30% of acetoacetanilide, and about 25% of a *substance*,

$C_{24}H_{22}ON_2$, m. p. 152°, colourless leaflets, which proves to be 1-*phenyl-2 : 4-dibenzyl 3-methyl-5-pyrazolone*. The explanation of this curious example of autobenzylation is very probably as follows. The pyrazole nucleus of one molecule of the phenylbenzylmethylpyrazolone is ruptured by the alkali, with the formation of the phenylbenzylhydrazide of acetoacetic acid, $CH_2Ph\cdot NH\cdot NPh\cdot CO\cdot CH\colon CMe\cdot OH$. Since the union of the benzyl group and the nitrogen atom in benzylated hydrazines is easily loosed, the hydrazide benzylates a second molecule of phenylbenzylmethylpyrazolone forming the substance, m. p. 152°, being itself converted into acetoacetanilide, an atom of nitrogen appearing ultimately as ammonia.

The proofs of the constitution of 1 phenyl-2 : 4-dibenzyl-3-methyl-5-pyrazolone are the following. In accordance with Knorr's experience of 1 : 2-disubstituted pyrazolones, it reacts with alkyl iodides to form ψ-alkyliodides, $CH_2Ph\cdot NI{\Large\lessgtr}{\scriptstyle\substack{NPh\cdot C\cdot OR \\ \| \\ CMe\text{-}C\cdot CH_2Ph}}$, which are decomposed by fusion or by aqueous alkalis into the original compound and alkyl iodide. The ψ-*methiodide*, $C_{25}H_{25}ON_2I$, decomp. 234°, pale yellow prisms, prepared at 100°, and the ψ-*ethiodide*, $C_{26}H_{27}ON_2I$, m. p. about 258—260° (decomp.), yellow, crystalline powder, prepared at 120°, are described. The former behaves abnormally with aqueous alcoholic potassium hydroxide in forming, not the original phenyldibenzylmethylpyrazolone, but a *substance*, m. p. 149°, colourless needles (*picrate*, m. p. 176°), the composition of which has not been determined. By heating with 10% sulphuric acid at 130°, 1-phenyl-2 : 4-dibenzyl-3-methyl-5-pyrazolone is decomposed into ammonia, aniline, benzoic acid, and benzylacetone. The authors show that *s*-phenylbenzylhydrazine by similar treatment at 135—140° yields ammonia, aniline, benzaldehyde, and benzoic acid.

In preparing the compound by the benzylation of 1-phenyl-3-methyl-5-pyrazolone, Stolz did not definitely prove the constitution of 1-phenyl-2-benzyl-3-methyl-5-pyrazolone. The authors have now done so, in consequence of the curious behaviour of the substance recorded above. It is converted into benzyl chloride and 5-chloro-1-phenyl-3-methylpyrazole by phosphoryl chloride at 140—150°. By heating in toluene with sodium in an atmosphere of carbon dioxide and subsequent treatment with ice and heating with dilute sulphuric acid, it yields aniline and benzylamine.   C. S.

Derivatives of Pyridazine and of Pyrrole. G. KARL ALMSTRÖM (*Annalen*, 1913, 400, 131—146).—With the exceptions of 4 : 5-diphenylpyridazine and 1 : 3 : 4-triphenylpyrrole, all the unknown diphenylpyridazines and triphenylpyrroles have been prepared.

3 : 5-*Diphenylpyridazin-6-one*, $N{\Large\lessgtr}{\scriptstyle\substack{CPh\cdot CH_2 \\ NH\text{—}CO}}{\Large\rangle}CHPh$, m. p. 154—155°, long needles, prepared by warming β-benzoyl-α-phenylpropionic acid and hydrazine hydrate in water, reacts with bromine in boiling glacial acetic acid to form 6-*hydroxy*-3 : 5-*diphenylpyridazine* $C_{16}H_{12}ON_2$, m. p. 183—184°, small needles. The latter is soluble in sodium hydroxide, and is converted by boiling phosphoryl chloride into 6-*chloro-*

3 : 5-*diphenylpyridazine*, m. p. 86—88°, which is reduced to 3 : 5-diphenylpyridazine, m. p. 139—140° (*platinichloride*,

$$2C_{16}H_{12}N_2,H_2PtCl_6,$$

yellow, crystalline powder; *picrate*, m. p. 137—138°), by hydriodic acid, D 1·22, at 160°.

In a similar manner, β-benzoyl-β-phenylpropionic acid and hydrazine hydrate yield 3 : 4-*diphenylpyridazin-6-one*, $C_{16}H_{14}ON_2$, m. p. 217—218°, from which, by methods similar to the preceding, have been successively prepared 6-*hydroxy*-3 : 4-*diphenylpyridazine*, m. p. 177—178°, 6-*chloro*-3 : 4-*diphenylpyridazine*, m. p. 110—111°, and 3 : 4-*diphenylpyridazine*, m. p. 106—107° (*platinichloride*, $2C_{16}H_{12}N_2,H_2PtCl_6$, dark yellow, microscopic plates; *picrate*, m. p 155—156°, dark yellow, crystalline powder).

β-Benzoyl-α-phenylpropionic acid and boiling aniline yield 1 : 2 : 4-*triphenylpyrrol-5-one*, $NPh{<}^{CPh:CH}_{CO-CHPh}$, m. p. 197—198°, faintly yellow, quadratic prisms. The latter becomes deep green when fused, and almost colourless again after solidification. By treating its solution in acetone and aqueous sodium hydroxide with acetyl chloride at 0°, 5-*acetoxy*-1 : 2 : 4-*triphenylpyrrole*, m. p. 172—173°, almost colourless plates (green when fused), is obtained, whilst phosphorus trichloride at 110—120° converts it into 5-*chloro*-1 : 2 : 4-*triphenylpyrrole*, m. p. 145—146, straw-yellow needles. The latter reacts with phosphoric and phosphoryl chlorides at 140° to form 3 : 5-*dichloro*-1 : 2 : 4-*triphenylpyrrole*, m. p. 152—153°, and is converted by hydriodic acid, D 1·22, and amorphous phosphorus at 150—160° into 1 : 2 : 4-*triphenylpyrrole*, m. p. 151—152°. 5-Chloro-1 : 2 : 4- triphenylpyrrole is converted by hot acetic anhydride and a few drops of concentrated sulphuric acid into 5-*chloro*-3-*acetyl*-1:2:4-*triphenylpyrrole*, $C_{24}H_{18}ONCl$, m. p. 188—189°, colourless plates, the position of the acetyl group being determined by the fact that the substance is converted into 5-*chloro*-3-*cinnamoyl* - 1 : 2 : 4 - *triphenylpyrrole*, $C_{31}H_{22}ONCl$, m. p. 150—151°, by warm alcohol, benzaldehyde, and sodium hydroxide.

β-Benzoyl-β-phenylpropionic acid and boiling aniline readily yield Klingemann's 1 : 2 : 3-triphenylpyrrol-5-one, m. p. 189°, from which 5-*chloro* -1 : 2 : 3 -*triphenylpyrrole*, m. p. 165—166°, and 1 : 2 : 3 -*triphenylpyrrole*, m. p. 176—177°, have been successively prepared. C. S.

Phenazine. FRIEDRICH KEHRMANN and EM. HAVAS (*Ber.*, 1913, **46**, 2820).—Methylphenazonium chloride, bromide, and nitrate can readily be isolated from concentrated aqueous solutions of the methosulphate (compare this vol., i, 298). C. S.

Salts of Azine Dyes. II. FRIEDRICH KEHRMANN, EM. HAVAS, and EUGÈNE GRANDMOUGIN (*Ber.*, 1913, **46**, 2802—2808. Compare this vol., i, 908).—The present results are communicated in consequence of the work of Ehrlich and Benda (this vol., i, 904) and of Pummerer and Gassner (*ibid.*, i, 991).

The colour change observed when many azonium bases are converted into salts is not necessarily indicative of constitutive change; in many cases it is due simply to a change in the auxochromic nature of the

amino-group during salt-formation. A number of dyes, such as *apo*-safranine, methyl*apo*safranine, 1:3-diaminophenylphenazonium bromide, 3:7- and 3:11-diaminophenylphenazonium chlorides, have been separately dissolved in alcohol and the solutions treated with regulated quantities of concentrated sulphuric acid; the amount of acid required for the production of different colours has been measured. The most important deductions made by the authors are as follows. The number of colours, with a given substance, agrees with the number of basic groups present, indicating that the individual basic groups possess different basicities, and that salt-formation proceeds step by step. Extraordinarily slight basicity is exhibited by all the salt-forming groups in a substance with the exception of one, by which the normal colour is conditioned; all other coloured salts exist only in quite strongly acidic solutions, and are immediately hydrolysed by dilution.

The influence of the position of an amino-group on the colour of the salts is also considered. An amino-group in the meta-position to the azine nitrogen is least influenced by hydrolysis. Its basic character is as strong as that of the amino-group in aniline, and a dye containing such a group forms a diacid salt even with only a slight excess of acid. An amino-group in position 11 (that is, in a phenyl nucleus), whether free or in a salt form, has practically no auxochromic influence. Also, such a group plays no part in strengthening the basicity, 3:11-di-aminophenylphenazonium chloride being in this respect similar to *apo*safranine.   C. S.

Action of Nitrous Acid on Ethyl Anilino-oximinoacetate.
LEOPOLD SEMPER and LEO LICHTENSTADT (*Annalen*, 1913, **400**, 302—332).—The substance $C_{10}H_{11}O_4N_3$, m. p. 169°, obtained by Jovitschitsch by the action of nitrous acid on ethyl anilino-oximino-acetate and described by him as ethyl phenyldioxatriazinecarboxylate (A., 1898, i, 93; 1899, i, 239; 1907, i, 98), has the composition $C_{10}H_9O_5N_3$ and m. p. 181·5° when quite pure, and proves to be *ethyl 7-nitro-1 : 2 : 4-benzoxadiazine-3-carboxylate,*

$$NO_2 \cdot C_6H_3 {<}{}^{NH \cdot C \cdot CO_2Et}_{O{-\!-}N} .$$
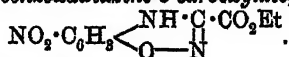
The yield of the substance is doubled by using 2 mols. of sodium nitrite instead of one (compare Jovitschitsch, *loc. cit.*). It forms a *potassium* derivative, $C_{10}H_8O_5N_3K$, dark red powder, and *benzoyl* derivative, $C_{17}H_{13}O_6N_3$, m. p. 165°, colourless crystals. Although ethyl oxanilate is obtained as a by-product in the formation of ethyl nitrobenzoxa-diazinecarboxylate, an intermediate product cannot be isolated; the same substance is also obtained, more slowly, by the action of nitric acid on ethyl anilino-oximinoacetate in glacial acetic acid.

By precipitating ethyl nitrobenzoxadiazinecarboxylate from acetone by water and treating the finely divided suspension with 0·2*N*-sodium hydroxide at 0°, an orange-yellow mass of the extremely unstable *7-nitro-1 : 2 : 4-benzoxadiazine-3-carboxylic acid,*

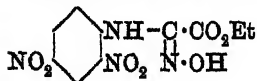$$NO_2 \cdot C_6H_3 {<}{}^{NH \cdot C \cdot CO_2H}_{O{-\!-}N} ,$$
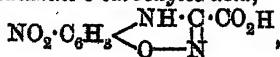
is obtained which can only be examined in the moist state. It decomposes at 118°, yielding nitrobenzoxadiazine, and regenerates the ester by treating its *silver* salt with ethyl iodide. *7-Nitro*-1 : 2 : 4-*benzoxadiazine*, $C_7H_5O_3N_3$, m.p. 240° (Jovitschitsch's phenyldioxatriazine, $C_7H_7O_3N_3$), is obtained from ethyl nitrobenzoxadiazinecarboxylate under the latter's conditions, except that $0.2N$-sodium hydroxide is employed; the *hydrochloride*, $C_7H_5O_3N_3$,HCl, m. p. above 300°, is a moderately stable, white substance.

By boiling for forty minutes with $0.2N$-sodium hydroxide (3 mols.), ethyl nitrobenzoxadiazinecarboxylate or nitrobenzoxadiazine is converted into *4-nitro-2-hydroxyphenylcarbamide*,

$$NO_2 \cdot C_6H_3(OH) \cdot NH \cdot CO \cdot NH_2,$$
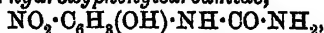
m. p. 203° (Jovitschitsch's phenyldihydroxydihydrodioxatriazine, $C_7H_9O_4N_3$ [A., 1907, i, 98]), which develops an olive-green coloration with alcoholic ferric chloride, yields 5-nitro-2-aminophenol and 4-nitrocatechol by prolonged boiling with 10% sodium hydroxide, and is converted at 210° into ammonia and nitrobenzoxazolone (nitrocarbonyl-*o*-aminophenyl), m. p. 241° (St. v. Chelmicky, A., 1891, 52). The preceding transformations suffice to establish the constitution of 4-nitro-2-hydroxyphenylcarbamide. The position of the nitro-group in ethyl 7-nitro-1 : 2 : 4-benzoxadiazine-3-carboxylate is proved by the reduction of the ester to 2 : 5-diaminophenol by boiling alcohol and stannous chloride.

The course of the reaction whereby ethyl anilino-oximinoacetate is converted into ethyl 7-nitro-1 : 2 : 4-benzoxadiazine-3-carboxylate by nitrous acid is readily explained in the light of Stoermer's researches on the simultaneous nitriting and oxidising action of nitrous acid on methylaniline and diphenylamine (A., 1899, i, 42). The nitrous acid attacks the aniline group and forms a substance (annexed formula), which, like other such dinitro-compounds, loses nitrous acid with the production of the nitrobenzoxadiazinecarboxylate.

Reactions similar to that exhibited by ethyl anilino-oximinoacetate and nitrous acid are also shown by substances containing the group $NHPh \cdot C(:NOH) \cdot$ attached to $\cdot COPh$ or $\cdot CO \cdot NH_2$. Thus the action of nitrous acid (2 mols.) on anilino-oximinoacetophenone yields *7-nitro-3-benzoyl*-1 : 2 : 4-*benzoxadiazine*, $NO_2 \cdot C_6H_3 \overset{NH \cdot C Bz}{\underset{O \longrightarrow N}{<}}$, m. p. 178° (decomp.), scarlet needles, which forms a bluish-red solution in alkalis, the solution losing the benzoyl group by long keeping, and yielding 7-nitro-1 : 2 : 4-benzoxadiazine. *Anilino-oximinoacetamide*,

$$NHPh \cdot C(:NOH) \cdot CO \cdot NH_2,$$
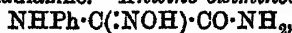
decomp. 192°, colourless needles, prepared from concentrated aqueous ammonia and ethereal ethyl anilino-oximinoacetate, reacts with nitrous acid (2 mols.) to form chiefly phenyloxamide; a by-product, however, is *7-nitro*-1 : 2 : 4-*benzoxadiazine-3-carboxylamide*,

$$NO_2 \cdot C_6H_3 \overset{NH \cdot C \cdot CO \cdot NH_2}{\underset{O \longrightarrow N}{<}},$$
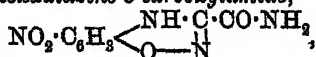
decomp. 240°, yellow crystals, the constitution of which follows from

the identity of the substance with the amide produced by the action of ammonia on ethyl 7-nitro-1 : 2 : 4-benzoxadiazine-3-carboxylate.

The action of nitrous acid (2 mols.) on oximinobenzanilide proceeds similarly and yet somewhat differently. Very little benzanilide is produced, the chief product being a *substance*, $C_{13}H_8O_3N_2$, m. p. 177—179°, which is very probably 5-nitro-1-phenylbenzoxazole (Fischer, A., 1906, i, 539); however, a small amount of a benzoxadiazine derivative is probably also formed, because the reaction product develops a deep violet-red coloration with alkalis.   C. S.

Preparation of Alkali Soluble Derivatives of Piaselenols [Benz*iso*selenodiazoles]. FELIX HEINEMANN (D.R.-P. 261412).— Benz*iso*selenodiazole, prepared by the action of selenous acid on *o*-phenylenediamine, is insoluble in water and alkalis, and the following compounds have been prepared with a view to eliminate this drawback.

3-*Hydroxybenzisoselenodiazole*, $C_6H_4ON_2Se$, yellowish-brown needles, is obtained when an aqueous solution of 3 : 4-diaminophenol hydrochloride is treated with sodium hydrogen selenite (1 mol.); it sinters and reddens at 200°, and has m. p. 209° (decomp.).

Benzisoselenodiazole-3-carboxylic acid, $C_7H_4O_2N_2Se$, m. p. 222—223°, a crystalline, rose-coloured powder, is prepared in a similar manner from 2 : 3-diaminobenzoic acid.
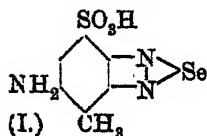
Benzisoselenodiazole-4-carboxylic acid is a colourless, crystalline powder with indefinite m. p., darkening at 260°, and decomposing violently at 290°.

(I.)

When 3-*p-nitro-o-sulphobenzeneazotolylene*-2 : 5-*diamine-4-sulphonic acid* is reduced it yields 2 : 3 : 5-*triaminotoluene-4-sulphonic acid*, and this on treatment with sodium hydrogen selenite gives rise to 4-*amino-3-methylbenziso*-selenodiazole-6-*sulphonic acid* (formula I); whilst naphthylene-1 : 2-diamine-5 : 7-disulphonic acid (A., 1906, i, 713) furnishes naphth*iso*selenodiazole-5 : 7-*disulphonic acid* (formula II), which is isolated as its crystalline *barium* salt by the addition of barium chloride to the reaction mixture.   F. M. G. M.

(II.)
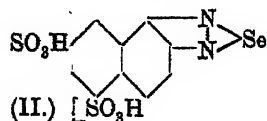
Rosinduline Isomerides, Nos. 16 and 17. FRIEDRICH KEHRMANN and MARCELIEN CORDONE (*Ber.*, 1913, 46, 2974—2979. Compare Abstr., 1899, i, 79).—The condensation of 3-acetylamino-1 : 2-naphthaquinone with phenyl-*o*-phenylenediamine has now been improved and much better yields of the two *iso*rosindulines obtained. The methods of preparation and separation of salts of the two acetyl compounds first formed are described.

10-*Acetylaminophenyliso*naphthaphenazonium *chloride*,

$$C_6H_4 \begin{array}{c} N(C_6H_5Cl):C——C_6H_4 \\ \diagdown \quad\quad\quad\quad\quad \diagup \end{array} OH,$$
$$N══════C(NHAc)$$
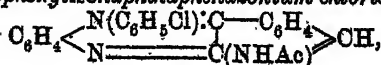
the form in which the substance is isolated, forms crystalline grains,

with a metallic lustre, is almost black, but yields a reddish-brown solution in water, and in alcohol a solution which is olive-green in thin layers and purplish-violet in thick layers. The *platinichloride* forms brownish-black crystals, and the *nitrate*, dark brown needles. The salts dissolve in sulphuric acid to form a violet solution, which, after heating and dilution with water, yields 10-*aminophenyl*isonaphthaphenazine (isorosinduline, No. 16); the *nitrate* of this forms small, olive-green needles; the *platinichloride* is an olive-green, crystalline precipitate.

5-*Acetylaminophenyl*isonaphthazonium nitrate, the form in which this substance is isolated, is an orange-red, crystalline powder; the *platinichloride* is a brick-red, crystalline precipitate, and the *chloride* crystallises from water in long, brick-red needles on salting-out with sodium chloride. All attempts to eliminate the acetyl group led to further decomposition of the substance. T. A. H.

Constitution of Safranine. EM. HAVAS and R. BERNHARD (*Ber.*, 1913, **46**, 2723—2727).—According to Barbier and Sisley (A., 1908, i, 225), phenosafranine is not a single chemical individual, but consists of a mixture of *indo*safranine (I.) and amino*apo*safranine (II.), commercial phenosafranine containing 85% of the latter compound.
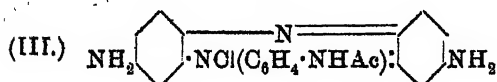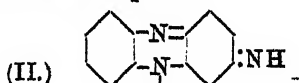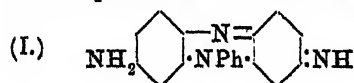
A compound of the constitution (II.) has now been prepared by the successive removal of one amino-group and the acetyl group from Ris's *p*-acetylaminosafranine (III.) (A., 1895, i, 148). It possesses the properties of an *apo*safranine, and, therefore, cannot form the main constituent of commercial phenosafranine.

Taken in conjunction with the work of Hewitt, Newman and Winmill (T., 1909, **95**, 577), the present results conclusively prove that phenosafranine is a single chemical individual and has the constitution represented in (I.).

The substances isolated by Barbier and Sisley are either hydrates or homologues, such as occur even in the purest commercial phenosafranine.

Acetylaminosafranine (III) is best prepared by the oxidation of di-*p*-aminodiphenylamine sulphate and acetyl-*p*-phenylenediamine by sodium dichromate in the presence of hydrochloric acid. It may also be obtained by oxidising a mixture of *p*-phenylenediamine, aniline and acetyl-*p*-phenylenediamine. In its appearance, tinctorial properties and absorption spectrum, it very closely resembles phenosafranine.

Aminosafranine is obtained in the form of its *sulphate* by boiling the preceding acetyl derivative with 10% sulphuric acid; the *platinichloride*, $C_{36}H_{32}N_{10}PtCl_8$, was analysed.

When treated with hydrochloric acid and sodium nitrite in alcoholic

solution, acetylaminosafranine is converted into *aminoaposafranine* (II), which forms a *platinichloride*, $C_{36}H_{30}N_8PtCl_6$, and is very similar to *apo*safranine.   F. B.

The Degradation of Uric Acid by Hydrogen Peroxide and an Iron Salt. KOHSHI OHTA (*Biochem. Zeitsch.*, 1913, **54**, 439—445). —By the treatment of uric acid with a boiling 30% solution of hydrogen peroxide in the presence of a ferric salt until all the uric acid was dissolved, the following products could be isolated. A crystalline substance, $C_3H_6O_3N_4$, which separated on cooling, with m. p. 235°, which is apparently carbonyldicarbamide ; a second crystalline substance separated from the mother liquors, which was not obtained pure and could not be identified. In addition, the following oxidation products were found : carbamide, oxalic acid and ammonia.

S. B. S.

Action of Aniline on Halogenated Phthaleins. VASSILI V. SCHARVIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 885—890) —The fact that anthraquinone derivatives containing hydroxyls, halogens, sodium or sulpho-groups in the α-positions are converted by the action of ammonia or primary amines into aminoanthraquinones which contain amino- or substituted amino-groups and act as stable violet-blue, blue or greenish-blue colouring matters, has led the author to apply this reaction to halogenated phthaleins.
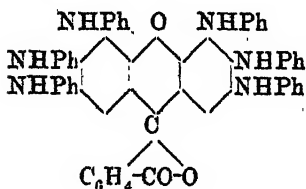
Treatment of eosin with excess of freshly-distilled aniline in a sealed tube at 180—200° yields the *hexaanilino-fluoran* (annexed formula), which forms a deep, violet-blue, amorphous powder and yields a bluish-violet alcoholic solution and a pure blue solution in acetic acid. It has no acidic properties, but is faintly basic in character, giving with acids blue salts which exist only in presence of a large excess of acid, and are completely hydolysed on dilution with water. In dilute alcoholic solution it is readily decolorised by hyposulphite, but gradually resumes its original colour in contact with air.

In a similar manner, tetrabromophenolphthalein and aniline yield *hexa-anilinophthalophenone*,
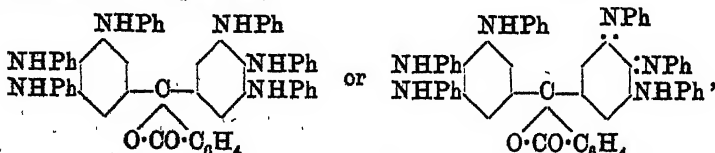
which is almost identical in colour and properties with the product obtained from eosin. This compound is accompanied by a bromo-derivative containing 4·16% of bromine, which would indicate a more complex molecule than that given above, since one bromine atom remaining in the molecule would correspond with 9·74% of bromine.

An analogous colouring matter was obtained by the action of aniline on chlorinated eosin containing halogen in the third benzene nucleus.

All the above compounds act as substantive colouring matters, and dye silk and wool violet-blue in an acid bath. The absence of the connecting oxygen atom between the two benzene nuclei of the substituted hexa-anilinophthalophenone renders the latter a somewhat less fast colouring matter than the fluoran derivative. These colouring matters may be converted into sulpho-salts soluble in water by treatment at 120° with fuming sulphuric acid containing 12% of sulphur trioxide.   T. H. P.

Preparation of Chlorinated Products in the Anthraquinone Series. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 262076). —Chlorinated products are obtained when diazotised aminoanthraquinones are treated with hypochlorites ; the *compound* from anthraquinone-2-diazonium sulphate is a pale yellow powder, decomp. 90°, whilst anthraquinone-2 : 6-bisdiazonium sulphate gives rise to a yellow powder.   F. M. G. M.

Saponification of Ethers of Hydroxyazo-compounds. G. CHARRIER and G. PELLEGRINI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 978—981).—These ethers can be readily saponified by acting on them with anhydrous aluminium chloride. When *o*-anisoleazo-β-naphthol is heated for a short time at 120—130° with four or five times its weight of aluminium chloride and the reaction mixture boiled with dilute sodium hydroxide, the *sodium* salt of phenol-2-azo-β-naphthol, $C_{16}H_{11}O_2N_2Na,3H_2O$, is obtained, and from it *phenol-2-azo-β-naphthol*, m. p. 193°, can be prepared. *o*-Phenetoleazo-β-naphthol behaves similarly.

p-Anisoleazo-β-naphthol yields *phenol-4-azo-β-naphthol*,

$$C_{16}H_{12}O_2N_2,$$

which crystallises in cantharides-green needles, m. p. 194°, and the same substance can be prepared similarly from *p*-phenetoleazo-β-naphthol.   R. V. S.

o-Aminoazobenzene. II. FELIX H. WITT (*Ber.*, 1913, **46**, 2557—2559. Compare A., 1912, i, 921).—As mentioned in the earlier paper, the researches of Gattermann and Wichmann (A., 1888, 829) indicate that the rearrangement of diazoaminobenzene must give rise to some *o*-aminoazobenzene besides the para-isomeride, because phenylazoiminobenzene, a dehydration product of the former, is present in the reaction product.

By maintaining the temperature below 40° during the rearrangement, the subsequent dehydration is checked, and up to 4% of the ortho-isomeride is found in the product and can be separated by recrystallisation of the mixture from benzene, in which the ortho-compound is much more soluble.

In common with other *o*-aminoazo-compounds (Goldschmidt and Rosell, A., 1890, 616; Goldschmidt and Poltzer, A., 1891, 839; Noelting and Wegelin, A., 1897, i, 155), *o*-aminoazobenzene condenses with aldehydes producing triazine compounds ; thus when warmed with

formaldehyde in solution in acetic acid to which a little concentrated hydrochloric acid has been added, it gives 2-*phenyl*-2 : 3-*dihydro*-1 : 2 : 4-*triazine*, $N\underset{\underset{NPh \cdot CH_2}{\diagup}}{\overset{\overset{-C_6H_4-}{\diagdown}}{<}}N$, yellowish-white needles, m. p. 210° (decomp.); a similar reaction with benzaldehyde in place of formaldehyde gives rise to 2 : 3-*diphenyl*-2 : 3-*dihydro*-1 : 2 : 4-*triazine*, $N\underset{\underset{NPh \cdot CHPh}{\diagup}}{\overset{\overset{-C_6H_4-}{\diagdown}}{<}}N$, very pale red crystals, decomp. at 215°.

<div align="right">D. F. T.</div>

Hydrolysis of Proteins with an Alcoholic Solution of Hydrogen Chloride. I. CHARLES WEIZMANN and GANESH SAKHARAM AGASHE (*Biochem. J.*, 1913, 7, 437—440).—The method is an attempt to shorten the usual process, by using a saturated alcoholic solution of hydrogen chloride from the beginning to serve both as a hydrolysing and an esterifying agent. The reagent is not so powerful as an aqueous solution for hydrolysis, as it contains less hydrogen chloride, and cannot be heated to so high a temperature. As expected, therefore, hydrolysis is not so complete. The proteins used, caseinogen and silk fibroin are only partly attacked, and the yield of separate amino-acids is poor.   W. D. H.

Indole Formation in the Hydrolysis of Proteins by Alkalis. E. HERZFELD (*Biochem. Zeitsch.*, 1913, 56, 82—94).—The indole was quantitatively estimated with the use of the colour reaction with the *p*-dimethylaminobenzaldehyde reagent, the spectrophotometric method of Herzfeld and Bauer being employed. It was found that small amounts of indole are obtainable from proteins on gentle warming with water. If proteins are treated with 0·5% sodium carbonate, indole is also produced; addition of hydrogen peroxide diminishes the amount, but addition of copper sulphate increases it. Similar results were obtained with 0·2% sodium hydroxide solution, but barium and calcium hydroxides gave smaller yields. It was found that larger yields were obtainable by increasing the concentration of the alkali hydroxide, the best results being produced with 9% sodium hydroxide; increase of the alkali concentration beyond this limit diminished the yield. One gram of protein was treated with 1000 c.c. of the alkaline solution. Under optimal conditions, tryptophan itself gives about 60% of the theoretical yield of indole. A pancreatic digestion product of caseinogen yielded 6·5% of the theoretical amount of indole, calculated on the assumption that this protein contains 0·8% tryptophan. Experiments were also arrived at with the object of ascertaining whether pyrrole and scatole are produced at the same time. The colour reactions employed for this purpose are described in some detail. No evidence of the production of these substances could be obtained.   S. B. S.

Separation of Proteins. III. Globulins. HENRY C. HASLAM (*Biochem. J.*, 1913, 7, 492—516).—The water-insoluble globulin of serum contains, or is closely associated with, rather more than 0·1

phosphorus %. About half of this belongs to a lecithin-like substance which amounts to 8—10% of the globulin freed from ψ-globulin. ψ-Globulin contains no phosphorus. By fractional salt precipitation, the details of which are given, the true globulin, ψ-globulin, and albumin can be satisfactorily separated.   W. D. H.

Racemisation of Proteins and their Derivatives Resulting from Tautomeric Change. II. The Racemisation of Casein. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, 15, 263—269).—It has been shown by Dakin (this vol., i, 208) that the treatment of gelatin by dilute alkalis at low temperatures produces racemisation, which is explained on the assumption of a ketol-enol tautomerism of the CH·CO-group. From the character of the amino-acids obtained by hydrolysis, it is claimed that some conception may be formed as to their position in the protein molecule, the occurrence of optically active amino-acids being taken as evidence of their being terminal groups. The preparation of a "racemised" casein is described, which is in fact a hydrolysis product of caseinogen (scission of phosphoric acid having taken place), which on hydrolysis yields inactive alanine, *d*- and inactive valine, *l*- and inactive leucine, *l*-proline and inactive tyrosine, phenylalanine, aspartic and glutamic acids, arginine, lysine, and histidine. As alkalis are used in the synthesis of polypeptides, it is presumed that with present methods it is not possible to synthesise a naturally-occurring protein.   S. B. S.

The Proline Fraction Obtained by the Hydrolysis of Caseinogen. The Isolation of Aminobutyric Acid. FREDERICK WILLIAM FOREMAN (*Biochem. Zeitsch.*, 1913, 56, 1—10).—From the proline fraction of the hydrolysis products, chloroform extracts a non-crystallisable, coloured substance. The residue after extraction with cold alcohol leaves a product which is aminobutyric acid. Further quantities of this substance can also be isolated from the extract in hot alcohol. The cold alcoholic extract when concentrated and treated with cold alcohol yields a precipitate, which is not entirely soluble in amyl alcohol at 60°. From this insoluble fraction, a glassy substance was obtained, which gives a characteristic copper salt, and contains only half its nitrogen in the form of an amino-group, and apparently a piperidine ring. In the same fraction there is also probably a basic substance. There appear to be also in the proline fraction other substances in which the nitrogen is not in the form of amino-groups. A method is also described for preparing fresh *l*-proline, which consists in treating an alcoholic solution of the proline fraction with freshly precipitated, dried and powdered copper hydroxide. The copper salt of the proline passes into solution.   S. B. S.

Colloidal Properties of Hæmoglobin. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1913, [v], 22, ii, 141—144).—By dialysis of the colouring matter of blood for four or five months, a pure product is obtained, which is gradually precipitated in the dialyser in very finely-divided form. It consists chiefly of methæmoglobin (95%).

It is almost insoluble in water and in neutral salts, but dissolves on addition of a trace of alkali, yielding a colloidal solution in which the colloid is electronegative. The product also dissolves in presence of a trace of acid, and the colloid in solution is then electropositive.

R. V. S.

The Combinations of Hæmoglobin with Oxygen and Carbon Monoxide. I. ARCHIBALD V. HILL (*Biochem. J.*, 1913, **7**, 471—480). —The oxygen and carbon monoxide dissociation curves of hæmoglobin differ according as salts and carbon dioxide are present or not. This has been explained on the theory that the simple molecules of hæmoglobin are aggregated into clusters. This explains all the facts provided two assumptions are made: (1) that the half-saturated molecules Hb_2O_2 and Hb_2CO are unstable, and change into either Hb_2, or $Hb_2(O_2)_2Hb_2(CO)_2$ or $Hb_2 \cdot CO \cdot O_2$; (2) that the half-saturated molecules combine much more readily with carbon monoxide than with oxygen. The first assumption can be explained as due to the fact that Hb_2 is $Hb \vdots Hb$, whilst Hb_2O_2 is $\vdots Hb \cdot Hb \vdots O_2$ with two unsaturated bonds which tend to combine at once with O_2 to form $O_2 \vdots Hb \cdot Hb \vdots O_2$. If these assumptions are justified, the deduction may be made that since carbon monoxide combines much more readily with $[Hb_2O_2$ than with Hb_2, hæmoglobin will take up more carbon monoxide at a given tension if a little oxygen is present than if it is completely absent. W. D. H.

The Combinations of Hæmoglobin with Oxygen and Carbon Monoxide. II. JOSEPH BARCROFT (*Biochem. J.*, 1913, **7**, 481—491). —The available data for the dissociation curves of blood agree very closely with the theoretical curves deduced from the following physical conceptions: (1) That the reaction is reversible:

$$Hb_n + nO_2 \rightleftharpoons Hb_nO_{2n};$$
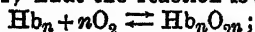
(2) that n is the average number of molecules aggregated together, its value depending on the nature and concentration of the electrolytes in solution; (3) that acids change the equilibrium constant of the reaction without altering the degree of aggregation; (4) that the action does not involve the breakdown and reformation of the aggregates; and (5) that unsaturated oxides are unstable and break up into hæmoglobin and saturated oxides. An entirely similar conception of carboxyhæmoglobin is supported by the available data. So far as the curves deduced from Hill's formula, $y/100 = Kx^n/1 + Kx^n$, can be distinguished from those held by Haldane and Douglas's more complex formula, the experimental evidence favours the former.

W. D. H.

Action of Alkyloxides on Hæmin and its Derivatives. II. Conversion of Hæmin into Mesohæmin. HANS FISCHER and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1913, **88**, 9—24. Compare this vol., i, 1006).—By the action either of potassium hydroxide in methyl alcohol or of potassium ethoxide on hæmin, the crystalline iron salt of mesoporphyrin, for which the name mesohæmin is suggested, is obtained. This transformation proves the presence of four pyrrole

nuclei in hæmin. Hæmatoporphyrin likewise yields mesoporphyrin on treatment with alkyloxides, but the quantity is small.

On reducing hæmatoporphyrin solutions with sodium amalgam until they became colourless, crystalline hæmatoporphyrinogen could not be isolated, but the solution of the leuco-base was used for physiological experiments. For two days after injection into rabbits it had no action, on the third day it had a sensibilising action indicating conversion into an active porphyrin. The physiological bearing of the inactivity of the leuco-base is discussed. E. F. A.

Blood Pigments. I. Degradation of Hæmins to the Porphyrins. RICHARD WILLSTÄTTER and MAX FISCHER (*Zeitsch. physiol. Chem.*, 1913, 87, 423—498).—I. *Constitution of Haemin.*—There is a certain resemblance between the porphyrins derived from hæmin and from chlorophyll; hæmatoporphyrin and mesoporphyrin, for example, having many points of similarity with phyllo-, pyrro-, rodo-, erythro- and rubi-porphyrins. On far reaching degradation of both classes of porphyrins by oxidation or reduction, similar simple pyrrole derivatives are obtained.

When hæmin and hæmatoporphyrin are heated with potassium hydroxide in methyl alcohol in presence of much pyridine, they are converted cleanly into crystalline porphyrins. Hæmatoporphyrin yields a product *haemoporphyrin* with four oxygen atoms; hæmin gives the complex iron compound of mesoporphyrin. Brief heating of the magnesium derivative of hæmoporphyrin with soda-lime eliminates the carboxyl groups and yields a substance identical with aetioporphyrin, $C_{31}H_{36}N_4$, from chlorophyll in composition, properties, spectrum and basic character. Accordingly, hæmoporphyrin has the composition $C_{33}H_{36}O_4N_4$, which assigns the formula $C_{33}H_{32}O_4N_4FeCl$ to hæmin instead of that usually adopted with 34 atoms of carbon. The new formula is in agreement with the analyses of hæmin derivatives and also with the older analyses of Küster (A., 1904, i, 357).


The basic skeleton of aetioporphyrin is composed of four pyrrole nuclei so united that eight hydrogen atoms are spared as compared with simple junction of the nuclei. The formulæ proposed by Küster, Piloty and H. Fischer are replaced by the above representation of aetioporphyrin.

Etiophyllin, $C_{31}H_{34}N_4Mg$, contains magnesium, presumably attached to all four nitrogen atoms. It is assumed that a vinyl residue is united

with one of the pyrrole nuclei to a *cyclo*butene ring. The position of this ring and of the substituting methyl groups is uncertain.

It is considered that hæmin contains a bridged ring, such as is known in several alkaloids, in two of the pyrrole nuclei, and it is represented as follows:
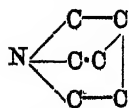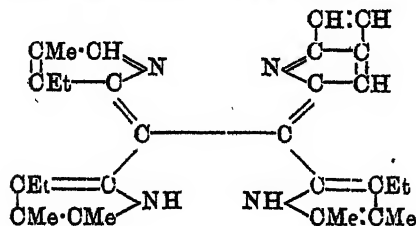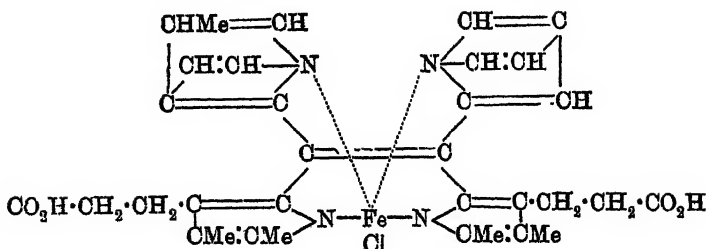
When hæmin is converted into hæmatoporphyrin, the two bridged rings are broken, $>$C:C$<$ becoming $>$C·C$<$, and one vinyl residue only becomes coupled with a carbon atom of the pyrrole nucleus. In mesoporphyrin the vinyl group CH:CH is saturated, although analysis does not allow the number of hydrogen atoms in this compound to be settled definitely. This conception is in harmony with the observed unsymmetric way in which the hæmin molecule alters on degradation.

II. *Intermediate products in the formation of hæmatoporphyrin.*—Aqueous hydrogen bromide saturated at 0° converts hæmin into the *dihydrobromide,* $C_{33}H_{84}O_4N_4FeBr_2$, which crystallises similarly to hæmin in large, obliquely-cut prisms of blackish-blue lustre, and forming a dark blue powder. The solution in concentrated sulphuric acid is a bluish-red.

Hydrogen bromide and acetic acid acting on hæmin yield a *trihydro-bromide,* $C_{33}H_{85}O_4N_4FeBr_4$. This forms a brownish-red powder.

When ether is added directly the hæmin has dissolved in the hydrogen bromide-acetic acid mixture; the *salt,* $C_{33}H_{36}O_4N_4Br_2,2HBr$, is obtained in bright red flakes: it is hygroscopic.

When sodium acetate is added to the solution in acetic acid and ether the colour changes from green to brownish-red, and finally the *monoacetate,* $C_{33}H_{36}O_4N_4Br·OAc$, is obtained as a brownish-red powder.

By the action of liquid anhydrous hydrogen bromide on hæmin the iron is eliminated, and a *bromide,* $C_{33}H_{39}O_4N_4Br_5$, obtained in lustrous, violet-red or red, crystalline leaflets.

Liquid hydrogen chloride allowed to act on hæmin for a few minutes only gives rise to a *compound,* $C_{33}H_{36}O_4N_4FeCl_5$, which forms a hygroscopic, lustrous, violet residue. Methyl alcohol converts it into a *dimethyl* ester, crystallising in lustrous, brown, rhombic platelets; it is less basic than any known methyl derivative of hæmatoporphyrin.

By the action of methyl alcohol on the pentabromide a *dimethyl ether dimethyl ester* was obtained, which crystallised in large, lustrous, double pyramids, m. p. 163°.

Hæmin dissolves in liquid hydrogen chloride in sealed tubes with a bluish-red coloration. The product could not be properly purified. Methyl alcohol converted it into a *tetramethyl* compound differing from that above. It crystallises in long, thin, brown, matted needles, m. p. 165°.

III. *Porphyrins with more than four oxygen atoms.*—A convenient method of obtaining hæmin from centrifugalised blood is described.

Hæmatoporphyrin, $C_{33}H_{38}O_6N_4$, previously only known in an amorphous condition, crystallises in lustrous, violet ounded plates, which are reddish-brown by transmitted light. The hydrochloride crystallises in needles which are olive-green under the microscope, but form a red powder. A *dimethyl* ester forms a lustrous, dark red, crystalline crust, m. p. 149°. A second *ester* formed on heating with weaker acid is an intense red powder, m. p. 121°.

The crystalline tetramethyl derivative (Küster and Deihle, this vol., i, 1004) has the molecular weight about 600, agreeing with the formula $C_{37}H_{46}O_6H_4$.

The *dimethyl ether*, $C_{31}H_{34}N_4(OMe)_2(CO_2H)_2$, crystallises in very fine, brownish-red, lustrous, prismatic plates, obliquely-cut and often forming twins resembling a swallow's tail. It sinters on heating, m. p. above 270°.

The *monoacetate*, $OAc \cdot C_{31}H_{34}N_4(OH)(CO_2H)_2$, is a bluish-violet powder.

By the action of liquid hydrogen chloride on hæmin and hydrolysis of the intermediate product, $C_{33}H_{37}O_4N_4Cl_6$, with acids, *hæminoporphyrin* is formed, having the composition $(C_{33}H_{37}O_5;N_4)_2$. When heated in a vacuum at 105° no water is eliminated as is the case with hæmatoporphyrin. It forms a heavy, dark violet powder consisting of metallic, rectangular platelets with rounded corners. The *trihydrochloride* forms bright red needles. The *methyl* ester is an intense red powder. Solution in saturated hydrogen bromide and dilution with water converts hæminoporphyrin into hæmatoporphyrin.

Another compound, *hæmidoporphyrin*, is obtained from hæmin hydrochloride on treatment with sodium acetate in warm acetone solution. It crystallises in very large prisms with a brownish-violet lustre, and behaves as an hydroxy acid.

All these compounds are differentiated by their basic properties as determined by their distribution between hydrochloric acid and ether (compare Willstätter and Mieg, A., 1907, i, 69).

IV. *Porphyrins with four oxygen atoms.*—Hæmoporphyrin is shown to have the formula $C_{33}H_{36}O_4N_4$. It is more strongly basic than the isomeric porphyrins obtained from chlorophyll. The *dimethyl* ester crystallises in obliquely-cut prisms with a number of twin forms.

On heating hæmin with potassium hydroxide in methyl alcohol and pyridine, the compound, $C_{33}H_{32}O_5N_4FeK_3$, is obtained in long, transparent, red prisms. Mesohæmin is obtained from this in lustrous prisms or thin, yellowish-brown plates. The *dimethyl* ester,

$$C_{33}H_{32}N_4(CO_2Me)_2 \cdot FeCl,$$
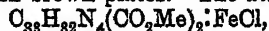
forms brown needles of metallic lustre.

Aetioporphyrin from hæmoporphyrin crystallises in small, reddish-brown prisms with oblique faces, m. p. 265° (decomp.). Despite minor differences, it is shown to be identical with the product derived from chlorophyll.   E. F. A.

The Saturated Fatty Acid of Kephalin. JAKOB PARNAS (*Biochem. Zeitsch.*, 1913, **56**, 17—20).—The only fatty acid obtained by the hydrolysis of kephalin with barium hydroxide was stearic acid. There is no evidence of the existence of a "palmitylkephalin"

in addition to the "stearylkephalin" as has been assumed by other authors.   S. B. S.

The Nitrogenous Constituent of Kephalin. MONTAGUE H. RENALL (*Biochem. Zeitsch.*, 1913, **55**, 296—300).—An improved process for the preparation of kephalin from ox and sheep brain is described. The disintegrated brain is treated with acetone, then with alcohol, and then with light petroleum. The crude kephalin from the latter extract is precipitated by alcohol, and is purified by precipitating from its solution in ether by alcohol, and from its solution in water by hydrochloric acid. Like the human brain, the brains of ox and sheep contain the nitrogen in the form of a primary base, and in ox brain the presence of aminoethyl alcohol could be detected.   S. B. S.

Phosphatides, particularly those in Egg-Yolk. JULIUS EPPLER (*Zeitsch. physiol. Chem.*, 1913, **87**, 233—254).—The products of hydrolysis of that portion of the phosphatides of egg-lecithin which is not precipitated by cadmium chloride consist of aminoethyl alcohol (compare Trier, A., 1912, i, 233) in addition to choline.

The phosphatide soluble in alcohol after complete extraction of egg-yolk with ether is a monaminomonophosphatide.

Comparison of the organic portion of cadmium chloride compounds with the original phosphatides shows a diminution in the amount of carbon, hydrogen and oxygen. Some elimination of fatty acid molecules has perhaps taken place.   E. F. A.

Plastein Formation. II. P. GLAGOLEV (*Biochem. Zeitsch.*, 1913, **56**, 195—208).—The grade of formation of more complex products, as measured by the Sörensen formaldehyde titration method, from dialysed hydrolysis products of proteins by dialysed ferments is not smaller than in the case of peptones containing the salt content of ordinary undialysed fermentation mixtures. The addition of salts, however, especially of sodium chloride, facilitates the formation of precipitates during plastein formation. The addition of sodium chloride up to 1·84%, and of calcium chloride up to 0·6%, exert no influence on the number of free amino-groups which disappear (as measured by Sörensen's method) during plastein formation; in fact, there is no definite relationship between the amount of precipitate formed during plastein formation and the amount of apparent synthesis, as measured by the diminution of free amino-groups. Plastein formation can also take place in absence of added hydrochloric acid in the presence of dihydrogen potassium phosphate.   S. B. S.

Action of Nuclease. P. DE LA BLANCHARDIÈRE (*Zeitsch. physiol. Chem.*, 1913, **87**, 291—309).—The gradual liquefaction of sodium α-thymus-nucleate is conveniently followed by viscometric methods. In this way nuclease may be identified, and its activity approximately determined. Nuclease has been proved to be present in the liver, thymus, pancreas, and in the seeds of the soja bean (*Glycina hispida*). The amount is largest in the pancreas. Nuclease is soluble in glycerol. It has a smaller affinity for colloids than trypsin, and may be protected

from tryptic digestion by treatment with colloids or animal charcoal. Yeast-nucleic acid, although differing in composition from thymus-nucleic acid, is hydrolysed by the nuclease of the thymus and the liver. Pancreas extract and the pancreatic secretion behave differently in decomposing nucleic acid. The liquefying and hydrolysing activities of nuclease are not parallel, from which it is inferred that two separate enzymes exist, or that the same enzyme contains two different active groups.　　　　　　　　　　　　　　　　　　　　E. F. A.

Studies on Amylases. V. Experiments on the Purification of the Amylase of Malt. HENRY C. SHERMAN and M. D. SCHLESINGER (J. Amer. Chem. Soc., 1913, 35, 1617—1623. Compare A., 1912, i, 815).—By extracting ground malt with two and a-half times its weight of water, dilute alcohol, or very dilute acid phosphate solution at as low a temperature as possible, with subsequent dialysis followed by fractional precipitation by alcohol or acetone, products have been obtained of diastasic power of 1800—2200 (Lintner's scale). The preparations resemble pancreatic amylase in appearance, but are less readily soluble in water; their solutions coagulate at 80°, giving large flocks.
　　　　　　　　　　　　　　　　　　　D. F. T.

The Action of Maltase on Starch. ZENON WIERCHOWSKI (Biochem. Zeitsch., 1913, 56, 209—219).—The saccharification of starch by the maltase of maize yields, in every stage, dextrose and soluble starch as the sole products of hydrolysis. The small amounts of dextrins, which yield a violet or red colour with iodine, owe their existence only to the presence of diastase. Maize diastase causes scission of all three kinds of carbonyl bonds in the starch with equal intensity, so that no dextrins are formed as intermediate products. Maize diastase appears, therefore, to be an ideal enzyme for the complete saccharification of starch.　　　　　　　　　　S. B. S.

Enzymes. Asymmetric Syntheses through the Action of Hydroxynitrilases. I. VERNON K. KRIEBLE (J. Amer. Chem. Soc., 1913, 35, 1643—1647).—The result obtained earlier by the author (A., 1912, i, 482) that a certain sample of emulsin when acting on amygdalin gave a residue of l-mandelonitrile, whilst its action on a mixture of benzaldehyde and hydrocyanic acid effected the formation of d-mandelonitrile can be attributed to the occurrence of varying quantities of two hydroxynitrilases in emulsin, one correlated with the d- and the other with the l-nitrile.

These two enzymes might be expected separately in plants which contain prunasin or amygdalin, and sambunigrin which are glucosides derived from the d- and l-nitrile respectively. An enzyme activating the combination of benzaldehyde and hydrocyanic acid to d-mandelonitrile was actually found in the leaves and bark of Prunus serotina, and in the leaves of the peach tree; the product obtained under its influence was not the pure d-isomeride, but the small quantity of racemic product present may have been due to the spontaneous combination of the constituents. The amount of racemic product given by emulsin cannot be explained in this way, and is probably to be ascribed to the concurrent action of two enzymes.

The leaf extract of the common elder, which contains sambunigrin, did not give rise to the formation of any optically active compound from benzaldehyde and hydrocyanic acid; whether this is to be explained by the presence of two enzymes concurrently producing *d*- and *l*-isomerides has still to be decided. D. F. T.

The Influence of Acids and Alkalis on the Diastatic Ferment during the Stages of Regeneration. M. J. GRAMENITZKI (*Biochem. Zeitsch.*, 1913, **56**, 78—81).—It has been shown by .the author that the properties of the diastatic ferment, which have been lost by heating, can, under certain circumstances, be regenerated on keeping. It is now shown that the regenerative process is inhibited by acid, but accelerated by alkalis in certain low concentrations. This is in direct contrast to the action of acids and alkalis on the extracted ferment, of which the former class of substances function as activators and the latter as inhibitors. S. B. S.
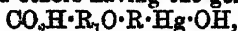
Preparation of Soluble, Stable Derivatives of 3:3'-Di-amino-4:4'-dihydroxyarsenobenzene. ANTON DERING (D.R.-P. 261542).—It is found that 3:3'-diamino-4:4'-dihydroxyarsenobenzene hydrochloride combines with albumin acids to furnish compounds which are soluble in water or alkalis, and are of therapeutic value. The preparation of the following *compounds* is described with .(1) sodium nucleinate; (2) sodium caseinate; (3) sodium protalbinate; (4) sodium. lysalbinate, and (5) from a mixture of sodium protalbinate and lysalbinate; the dry substances are yellow, amorphous masses, the alkali salts greenish-grey lamellæ. F. M. G. M.

Preparation of Nuclear-substituted Mercury Derivatives of Aryloxy-fatty Acids and their Salts. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 261229).—*Mercurithymolacetic anhydride* (annexed formula), a sand-like powder, is obtained when mercuric acetate and thymolacetic acid are heated together in aqueous-alcoholic solution at 70°.
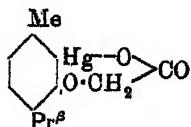
a-*Guaiacolpropionic acid*, m. p. 55°, is prepared by the action of sodium guaiacol on a-bromo-propionic acid; on heating with mercuric acetate it gives rise to *mercuri-a-guaiacolpropionic acid*. These compounds are of therapeutic value, and others having the general formula

$$CO_2H \cdot R_1O \cdot R \cdot Hg \cdot OH,$$

where R is phenyl, naphthyl or their substituted derivatives, and R_1 alkyl or substituted alkyl groups, are also discussed.

F. M. G. M.

Preparation of Soluble Silver Salts of Mercury Derivatives of Hydrocarbons. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 261875).—When the insoluble silver salts of the substituted mercury derivatives of hydrocarbons are treated with the alkali salts of amphoteric or faintly acidic substances they furnish soluble additive

compounds, and the following have been prepared: from hydroxy-mercurithymoxyl acetate with sodium diethylbarbiturate and from silver hydroxymercuribenzoate with sodium succinimide.

F. M. G. M.

Physiological Chemistry.

Physiological Observations following Descent from Pike's Peak to Colorado Springs. EDWARD C. SCHNEIDER (*Amer J. Physiol.*, 1913, **32**, 295—308).—The return of the blood to a normal state after descent from a great altitude is very slow. Details regarding the percentage of hæmoglobin, red corpuscles, blood volume, pulse rate, alveolar carbon dioxide pressure, etc., are given. The respiratory capacity is not greater in men who live high up than those of similar physique at sea level. W. D. H.

The Respiration of Pulverised Insects. FRED. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1913, **56**, 35—49).—Pulverised insects exhibit a high respiratory exchange, which in certain cases is as large at 40° as that of the living animals, but in others (flies, silk-worm moths) markedly smaller. The respiratory exchange increases with rising temperature up to 30°, and remains from this point constant until about 55°. A slight alkalinity increases in some cases the respiratory exchange, but higher alkalinities exert an inhibitory action, notably on the carbon dioxide production. In acid media both the oxygen consumption and carbon dioxide production are diminished. The gas-exchange takes place both in hypo- and iso-tonic solutions, and is not affected by addition of disodium hydrogen phosphate. It is not much larger in an atmosphere of oxygen than in one of air, and is not influenced by the addition of mammalian blood or of pnein. The addition of trypsin only depresses the respiratory exchange to a small extent. The alcohol and acetone preparations of pulverised insects also exhibit a distinctly high respiratory exchange. Attention is called by the authors to the differences between the respiratory exchanges of pulverised insects and of mammalian tissue; the former are to be ascribed to the presence of oxydases of unknown character.

S. B. S.

The Intensity of the Respiratory Exchanges of Insects. FRED. BATTELLI and LINA STERN (*Biochem. Zeitsch.*, 1913, **56**, 50—58). —The oxygen consumption, carbon dioxide production, and respiratory quotients of cockroaches, silk-worms, and of flies in various stages of development are tabulated. There is an increased respiratory exchange with increasing temperatures. This is also greater in the fully developed insects than in the larvæ, and the latter are more active than the chrysalis. S. B. S.

The Cholesterol and Cholesterol Ester Content of the Blood of Various Animals. FELIX KAUDERS (*Biochem. Zeitsch.*, 1913, **55**, 96—100).—A series of analytical results obtained by the Windaus digitonin method is tabulated. The cholesterol and cholesterol esters were estimated both in the serum and corpuscles.

S. B. S.

Lactic Acid in Blood. WALTER GRIESBACH and SIEGFRIED OPPENHEIMER (*Biochem. Zeitsch.*, 1913, **55**, 323—334).—The formation of lactic acid from various substances by the action of blood corpuscles was investigated. Dextrose, lævulose, mannose, and galactose were found to be capable of forming this acid, whereas arabinose and glucoheptose were not. Inositol was in the majority of cases found to be inactive, but in two cases a slight increase of lactic acid was found. Alanine was indifferent, and glycerol was also generally indifferent, although in one case it gave rise to a considerable amount of acid. It appears as if the same tissue from different individuals of the same species shows an inconstant behaviour as regards the formation of lactic acid from the same substance.

S. B. S.

Method for Extraction of Amino-acids from Different Constituents of the Blood. A. COSTANTINO (*Biochem. Zeitsch.*, 1913, **55**, 419—424).—One hundred c.c. of the blood or serum are mixed with 500 c.c. of 2% mercuric chloride solution containing 0·8% hydrochloric acid. The proteins are thereby precipitated. An aliquot part of the filtrate, obtained after centrifugalisation, is evaporated in vacuum after addition of magnesium oxide (in order to separate ammonia) to a small bulk, in which the formalin titration process is carried out. This is done after addition of solid barium chloride and hydroxide, filtering off the precipitate, and neutralising the filtrate to azolitmin. Where very small amounts of amino-acids are present, a certain known amount is added before these manipulations, so that larger amounts of alkali are required for titration.

S. B. S.

The Normal Sugar Content of the Blood of Rabbits and Dogs. ADOLF LOEWY and SIEGFRIED ROSENBERG (*Biochem. Zeitsch.*, 1913, **56**, 114—116).—The statement has often been made that the sugar in the blood of rabbits occurs abnormally as a result of the treatment of the animals (binding, exposing the arteries, etc.). The authors now show that a similar phenomenon can be observed in dogs. It was noticed, furthermore, that the blood removed under conditions of local anæsthesia (novocaine) contained less sugar than that removed from the same animals without anæsthesia, and that pain probably has some influence on the abnormally high sugar content in the blood of animals.

S. B. S.

Blood Glycolysis: its Extent and Significance in Carbohydrate Metabolism. The Supposed Existence of "Sucre virtuel" in Freshly Drawn Blood. JOHN J. R. MACLEOD [with A. M. WEDD] (*J. Biol. Chem.*, 1913, **15**, 497—514).—Unclotted

(hirudin) and defibrinated blood have the same glycolytic power, but potassium oxalate has a depressing action. The rate of glycolysis varies greatly, but in the mean about half the sugar disappears, in two and a-half hours at 40°. This is a function of the corpuscles. If much dextrose is added to the blood, the process may be depressed. The rate is the same in diabetic blood. The destruction of sugar in the blood in the intact animal is an almost negligible fraction of the total glycolysis. W. D. H.

Permeability of Blood Corpuscles for Amino-acids. A. COSTANTINO (*Biochem. Zeitsch.*, 1913, **55**, 411—418).—By suspending blood corpuscles in serum in which an excess of amino-acid had been dissolved, and estimating the nitrogenous substances titratable in the presence of formalin, it was found that these diminished in the serum and increased in the corpuscles. From this it follows that the latter are permeable to amino-acids, but, as experiment showed, only up to a certain limit. This corresponded nearly with the amount of amino-acids in the corpuscles of a dog at the time of digestion of food, that is, 45 mg. nitrogen per litre of corpuscles. The amount reached did not differ greatly whether asparagine, the acid hydrolysis products of caseinogen, or glycine was added to the serum. S. B. S.

The Amino-acid Nitrogen, which can be Estimated by the Formalin Method, in the Blood Corpuscles and Serum of Fasting and Fed Animals. A. COSTANTINO (*Biochem. Zeitsch.*, 1913, **55**, 402—417).—The author, by various methods described in some detail, is able to confirm the presence of amino-acids in the blood. The amount in fasting animals is less than that in fed animals, although there is no difference in the amounts in the serum in animals at different stages of nutrition. From this it follows that the excess of amino-acids in the blood of fed animals over that in blood of fasting animals is present in the corpuscles, which must consequently be permeable to these acids. The content of both serum and corpuscles in amino-acids is the same in all parts of the circulation, and this fact negatives the supposition of the deaminisation of the digestion products in the intestinal wall. Lymph contains only a small amount of nitrogen titratable in the presence of formalin. S. B. S.

The Influence of Lipoids on the Coagulation of Blood. FRIEDRICH RUMPF (*Biochem. Zeitsch.*, 1913, **55**, 101—115).—Lipoid emulsions (prepared from ox-brain) hasten the coagulation of oxalate plasma, but only to a slight extent, which is quantitatively far below the action of tissue extracts. There is no species specificity in this action. Plasma which has been deprived of its lipoids by light petroleum will only coagulate after addition of lipoids. This fact does not prove, however, that thrombokinase is a lipoid. The statement of Bordet and Delange, that lipoids, like tissue juices, cause the development of large quantities of thrombin in serum, appears to be incorrect, as the acceleration of clotting

4 *p* 2

caused by the former is insignificant compared with that caused by the latter (30 : 600). Peptone and hirudin bloods can be made to clot by tissue extracts, but not by lipoids. The lipoids, therefore, do not appear to be the actual active agents, although they do play some part in the clotting process. It seems therefore advisable to retain the term thrombokinase for the active substance of tissue juices.   S. B. S.

The Nature of Thrombin and Anti-thrombin. BERTRAM J. COLLINGWOOD and M. T. MACMAHON (*J. Physiol.*, 1913, **47**, 44—53). —Thrombin is destroyed by heat (50—60°), by acid, alkali, and trypsin. After destruction of Gamgee's thrombin, thrombokinase is still present; this preparation also contains fibrinogen. Antithrombin is destroyed by heat (60—65°) and by acid. It will act only in an alkaline medium; neutralisation inhibits, but does not destroy it. The rate of action of antithrombin varies directly with temperature in contrast with thrombin. It is suggested that thrombin is a protein, that antithrombin is a proteolytic enzyme, and that fibrin is a combination of thrombin and fibrinogen.
                                                           W. D. H.

The Properties of Rabbit's Serum after Treatment of the Animals with Emulsin. KOHSHI OHTA (*Biochem. Zeitsch.*, 1913, **54**, 430—438).—When rabbits have been immunised by several injections of emulsin, their serum exerts a greater inhibitory action on the action of the ferment than the serum of normal animals. This difference of action is, however, only marked when the serum is present in sufficient quantities. If d-galactose and dextrose are incubated together in the presence of immune serum, there is evidence of the formation of a disaccharide, of which small quantities of a phenylosazone could be isolated.   S. B. S.

Hæmolytic Action of Cyclamin–Cholesterol Mixtures. ERNST H. RIESENFELD and H. LUMMERZHEIM (*Zeitsch. physiol. Chem.*, 1913, **87**, 270—290).—On mixing equivalent quantities of cyclamin and cholesterol, a mixture is obtained in which the hæmolytic action of cyclamin is only partly suspended. Further addition of cholesterol has the effect of lessening the poisonous action. It is therefore inferred that the cyclamin-cholesterol complex is dissociated in solution. If the hæmolytic action of any cyclamin-cholesterol mixture is regarded as a measure of the amount of free cyclamin, it is possible to determine the dissociation constant K of the cyclamin-cholesteride, provided that the total amount of cyclamin and cholesterol in the mixture is known. Constant values for K are obtained by this method so long as the same blood solution is used, but different values of K are obtained with different blood solutions, owing probably to the presence of the serum. The serum has the property of lowering the hæmolytic activity of cyclamin, but acts quantitatively in a very variable manner.   E. F. A.

The Hæmolytic Lipoids of the Organs and the Influence on them of Administration of Dextrose. ARNO KIRSCHE (*Biochem. Zeitsch.*, 1913, 55, 169—188).—Various investigators have shown that the liver contains hæmolytic lipoids, which appear to have a special pathological significance in certain diseases, such as pernicious anæmia. The conception is now advanced that in fatty degeneration of the liver the lipoids are of two-fold origin, namely, those due to degeneration of the cell material itself, and those due to infiltration. To the former class only is to be ascribed the hæmolytic activity. This hypothesis has been tested in the following way: In a number of rabbits fatty degeneration was produced by the following methods: starvation, phloridzin, acute and chronic poisoning with tolylenediamine, maintenance of the animal at high temperatures, post-mortal autolysis. The lipoids were obtained from the liver by heating this organ with alcohol, then extracting with ether, and precipitating the lecithins from the ethereal extract by acetone; after distillation of the ether–acetone mixture the residue was weighed and used for experiment in methyl-alcoholic solution. The hæmolytic value of this solution was then determined. It was found that in all cases, both the quantity of extract and its hæmolytic value were increased in cases of fatty degeneration, especially in that produced by autolysis. Now it is supposed that administration of dextrose inhibits infiltration. A series of experiments similar to the above was carried out with this addition. If the action of sugar is correctly interpreted, then the lipoids derived from the sugar-fed animals should contain relatively larger amounts of fats derived from the cell degeneration, and consequently a higher hæmolytic value. This was actually found to be the case. Attention is also called to differences in the fatty-degenerated livers produced by different methods. S. B. S.

Digestion and Absorption under Normal and Pathological Conditions. EFIM S. LONDON (*Zeitsch. physiol. Chem.*, 1913, 87, 313—370).—This is a series of short papers on various aspects of the subject carried out on fistula dogs by London's methods.

I. *General Remarks*. E. S. LONDON.—Introductory.

II. *Does Absorption Occur in the Stomach?* J. S. TSCHEKUNÒV. —Many previous authors have stated that absorption occurs in the stomach. In the present experiments finely-divided meat alone or mixed with gliadin was given by the mouth, or solution of dextrose or sodium chloride by the gastric fistula. The material which left the stomach contained the same amount of sugar as given, and protein substances entirely leave the stomach with an accession of nitrogen. In no case was there a deficit in the food material introduced. The proteins were not much broken up in the stomach (amide nitrogen = 11—18%).

III. *Absorption Products of Protein*. N. A. DOBROVOLSKAJA.— Two hundred c.c. of a 5% solution of alanine was placed in the intestine. In five minutes excess of amide nitrogen was found in the blood of the jugular vein. During digestion, the amide

nitrogen rises in the portal blood; the rise in the general blood stream is smaller. In no case did the blood give a biuret reaction.

IV. *The Amount of Amide Nitrogen in the Peripheral Blood during Digestion.* A. D. VOLKOV.—In all stages of digestion the jugular blood contains a small excess of amide nitrogen (almost 4 mg. per 100 c.c. of serum).

V. *The Influence of Surgical Changes in the Stomach on Digestion.* S. F. KAPLAN.—The pyloric section of the stomach plays an important rôle in the proper evacuation of the organ. Hydrochloric acid stimulates the fundus, and inhibits the pylorus. Sodium hydrogen carbonate also stimulates the fundus. Partial extirpation of the fundus hastens the emptying of the stomach. Observations on the rate of emptying an "hour glass" stomach are also given.

VI. *Digestion in Intestinal Resections.* P. P. BRJUCHANOV.— Resection of the jejunum makes no difference on the course of excretion of the constituents of the chyme through a fistula, but the rate of output is raised. The complete compensation for the defect does not, however, occur in the upper section of the digestion canal; the ileum takes no special share in the work of compensation; the main share falls on the large intestine. Opium and tannalbin do not lessen, but increase, the discharge through the fistula. Similar details are given in reference to removal of other parts of the bowel.

VII. *The Course of Digestion of Anomalous Constituents of the Gastric Contents.* R. S. KRYM.—Preliminary digestion of the meat-powder given does not hasten the emptying of the stomach. Excess of hydrochloric acid inhibits it.

VIII. *Digestion of Peptonised Milk.* Z. O. MITSCHNIK.—In vitro, peptonised milk is more rapidly digested by gastric, but not by pancreatic, juice. In dogs it causes an increase in the flow of bile. In weakly children, and certain pathological conditions, its use is advised. Further work is in progress.

IX. *The Physiological Importance of the Omentum.* M. R. GILLELS.—The experiments confirm the conclusion that the omentum is of importance, but compensation by the mesentery takes place. Further work is in progress.

X. *The Digestive Glands in Normal and Defective Digestion.* P. P. BRJUCHANOV.—The injection of an aqueous solution of Witte's peptone into the jejunum increases the excretion of bile; this is not affected by acidification of the solution with hydrochloric acid, but if the solution is made alkaline by sodium hydrogen carbonate, it stops the bile flow. Neutral or alkaline peptone solution has no effect on the pancreas, but hydrochloric acid excites a flow of pancreatic juice.

XI. *Maximal Reduction of the Alimentary Tract.* With S. F. KAPLAN.—Experiments are recorded which show how greatly the canal may be reduced without serious harm in dogs. Large amounts of the small intestine, and the whole colon were removed, and the dogs were in good condition months afterwards.   W. D. H.

Absorption of Yeast-Nucleic Acid after Extensive Resection of the Small Intestine in Dogs. JUNICHI MAYESIMA (*Zeitsch. physiol. Chem.*, 1913, **87**, 418—122).—Removal of the greater part of the small intestine in dogs has no practical effect on the absorption of yeast-nucleic acid. Whether this is due to the remnants of the intestine, or to the activity of micro-organisms, is uncertain.   W. D. H.

The Influence of Chronic Insufficient Nutrition on Metabolism. NATHAN ZUNTZ, S. MORGULIS, and M. DIAKOV (*Biochem. Zeitsch.*, 1913, **55**, 341—354).—A dog was kept over a prolonged period (more than a year) on a diet insufficient for the energy needs of the organism, during which time the weight sank from 10 to 4·19 kilos. The animal then died of inanition. The caloric value of the food administered (rice and meat) was controlled during the whole time, and repeated measurements of the respiratory exchanges were made; the nitrogen excreted was also repeatedly estimated. It was found that the energy consumption per square metre of surface sank during this period from 931 cal. per 10 kilos. of weight to a minimum of 631 for half that body weight, and rose again towards the end of the life of the animal to 921 calories for a weight of 4·1 kilos. There was no indication of a gradual accommodation of the energy consumption to the diminished food supply.   S. B. S.

Metabolism during Pregnancy and Lactation. LUDWIG DIENES (*Biochem. Zeitsch*, 1913, **55**, 124—133).—The gaseous metabolism of a tracheotomised dog during pregnancy and lactation was carried out by a method, described in some detail, based on the Regnault-Reiset principle. The results indicate that there is a large increase in the metabolism during the later stages of pregnancy. During lactation, on the other hand, the increase in the metabolism is relatively small.   S. B. S.

The Carbohydrate Metabolism of the Isolated Heart–Lung Preparation. S. W PATTERSON and ERNEST H. STARLING (*J. Physiol.*, 1913, **47**, 137—148).—Starling and Knowlton stated that the diabatic heart is unable to utilise sugar as well as the normal heart. Furthermore accurate work has shown that this is not the case. The main purport of the present paper is to withdraw the former conclusions, and explain Maclean and Smedley's results, which seemed to confirm it; the glycogen of the heart muscle is a varying and disturbing factor, which may account for certain discrepancies. The view that the primary factor in diabetes is an absence of the power of the tissues to consume sugar is abandoned.   W. D. H.

The Rate of Resorption of Proteins and their Degradation Products from the Small Intestine. HERMANN MESSERLI (*Biochem. Zeitsch.*, 1913, **54**, 446—473).—The experiments were

carried out on a dog with a Thiry-Vella fistula. The various products under investigation were introduced into the fistula, and removed after a definite interval by a method described by the author. The amount of resorption of proteins and degradation products was determined by estimations of nitrogen. All experiments were carried out on the same animal. The amounts of genuine proteins taken up in ten minutes may be represented by the following numbers: Serum, 20; gliadin, 16; caseinogen, 12; hæmoglobin, 8. The less degraded proteins, such as peptones, are resorbed more rapidly than the products of complete acid hydrolysis. This fact indicates that the proteins are not degraded completely in the small intestines. During a diet poor in proteins, the resorbability of various proteins progressively diminished, but increased again when the animal reverted to a protein-rich diet. This phenomenon was observed, however, only in the first experiments. In later experiments the resorption was less during the subsequent period of rich protein diet. This is probably due to the fact that after the various treatments to which the animal had been subjected, the cells of the intestine had lost their physiological functions as regards the resorption of nitrogenous products. Their capacity for taking up sugar remained, however, unimpaired.

S. B. S.

The Pentoses as a Source of Energy in the Animal Organism. P. Schirokich (*Biochem. Zeitsch.*, 1913, **55**, 370—392). —The experiments were carried out with *l*-arabinose prepared from cherry-gum. It was found that the addition of this carbohydrate to a given basal diet caused very little rise in the respiratory quotient, and about half of the amount ingested was excreted unchanged in the urine. When dextrose was given in corresponding quantities, a certain increase in the respiratory quotient could be ascertained. The increased oxygen consumption, which takes place normally after a meal, is slightly diminished by the addition of dextrose to the diet, and largely diminished by arabinose.

S. B. S.

The Biological Significance of Phosphorus for the Growing Organism. I. The Influence of Phosphorus on the Growth of Animals and on the Phosphorus and Nitrogen Metabolism. M. Masslov (*Biochem. Zeitsch.*, 1913, **55**, 45—62).—The rate of growth of puppies from three different litters on diets rich and poor in phosphorus was investigated. As basal diets a gruel containing rice, albumin and sugar, cow's milk alone, cow's milk in which the caseinogen was replaced by egg-albumin, which was therefore poor in phosphorus content, and mixed diets of meat, milk, and porridge were employed. The animals were found to thrive only on the mixed diet. The animal fed on milk lived longer than the other animals, but even in this case it finally died of inanition. Phosphorus was added in other experiments after a period on the phosphorus-poor basal diets, in the form either of lecithin, glycerophosphate, or inorganic phosphate. The addition of

lecithin caused a temporary improvement of condition, but in this, as in all the other cases in which phosphorus was added, the animals finally succumbed. The rate of growth when the animals were transferred from a normal to a special diet was not affected immediately, but loss of weight occurred only when they had been a certain time on the abnormal diet. The experiments here recorded do not show conclusively whether the normal growth is due to phosphorus in any special form of combination, or to some other factor. S. B. S.

The Biological Significance of Phosphorus for the Growing Organism. II. The Content of Phosphorus and Intracellular Ferments in the Various Organs. M. MASSLOV (*Biochem. Zeitsch.*, 1913, **56**, 174—194).—The author gives the content in inorganic, organic, and phosphatide phosphorus of the organs of the animals fed by the methods described in the former paper (preceding abstract). The chief loss of the organs during a period of phosphorus starvation is in the inorganic phosphorus. The least loss is in the "organic" phosphorus (nucleoproteins, etc.). The lipoid phosphorus is less stable. Heart and brain do not under any conditions suffer loss in phosphorus, whereas the liver, intestines, muscles, bone-marrow, and kidneys lose considerable quantities during phosphorus starvation. When this loss attains certain limits, the animals die. The only phosphorus compound which produced, when added to the phosphorus-poor diet, an increase in the phosphorus-content of the organs, was lecithin. As regards the intracellular ferments, it was found that on a mixed milk and meat diet, there was a general increase in the fermentative energy of the organs, especially of the lipolytic, amylolytic, and diastatic energy. The development of the catalytic and nucleolytic energies was less marked. Under the influence of phosphorus starvation, not only is there no increase of fermentative energy of the organs, but in certain cases there is a distinct diminution. S. B. S.

The Soft Roes of Fish as Foodstuff for Man. JOSEF KÖNIG and J. GROSSFELD (*Biochem. Zeitsch.*, 1913, **54**, 333—350).—The soft roes from herring and carp were submitted to chemical examination by methods described in some detail, and found to contain meat bases (xanthine and creatinine) and free amino-acids in addition to the protamines, which exist combined with nucleic acid. The fatty substances consist to a large extent of lecithin (20·2—20·7%) and cholesterol (11·2—17·9%). S. B. S.

The Hard Roes of Fish as Foodstuff for Man. JOSEF KÖNIG and J. GROSSFELD (*Biochem. Zeitsch.*, 1913, **54**, 351—394).—The eggs of fish contain a relatively small amount of water as compared with hen's egg; they contain also meat bases, amino-acids, together with ichthulin, as chief protein (which is insoluble in water), albumin, and quantities of fat, which vary in the different species. All the roes investigated contain xanthine substances and creatinine. Xanthine and hypoxanthine were isolated, and the presence of the

following amino-acids was proved, viz., taurine, *l*-tyrosine, and glycine. The presence of thymine was also determined. The proteins contain relatively large quantities of sulphur and phosphorus. No protamines could be isolated from the ichthulins. These substances, on hydrolysis with sulphuric acid, yield purine bases, as Hammarsten and Levene and Mandel have already shown. The ichthulins and albumins yield, furthermore, on hydrolysis, tyrosine, leucine, arginine, histidine, and small quantities of lysine. The ichthulin of carp yields also glutamic acid. The fats contain large quantities of lecithin (up to nearly 60%), and not inconsiderable amounts of cholesterol (3·9—14%). The roes which are poorest in fats contain the largest amounts of lecithin. Caviare and other roes contain free acids, which increase in amount on putrefaction. Of the mineral matter, the acid ions are in excess of the basic ions, as the sulphur and phosphorus are in organic combination.

S. B. S.

Chemical Differentiation of the Central Nervous System. III. Chemical Differentiation of the Brain of the Albino Rat during Growth. Waldemar Koch and (Miss) Mathilde L. Koch (*J. Biol. Chem.*, 1913, **15**, 423—448).—The principal chemical changes which occur in the rat's brain during growth are: a decrease in water which begins before medullation sets in; a relative fall in protein due to appearance of lipoids. The lipoids which appear with medullation are cerebrosides and sulphatides. The phosphatides increase before medullation, and occur both in cells and sheaths. Organic sulphur compounds diminish relatively with age, whilst the colloidal sulphur rises. The increase of colloidal matter, which is relatively inactive supporting matter, is one factor in the slowing of metabolism which characterises senescence. W. D. H.

The Action of Ions and Lipoids on the Frog's Heart. A. J. Clark (*J. Physiol.*, 1913, **47**, 66—107).—An excised frog's heart after perfusion for a few hours passes into a hypodynamic state, and is more readily affected by ionic changes in the fluid perfused. It is improved by increase in the calcium relative to sodium and potassium, and not much improved by increase in hydroxyl ions. The hypodynamic state is caused by a loss of power to combine with calcium. The hydrogen ion concentration must be within narrow limits ($10^{-6·7}$ and $10^{-8·5}$), and a buffer must be present to stabilise the concentrations. A slight increase of carbon dioxide, amino-acids, glycogen, and sugars to a less extent benefit the hypodynamic heart. But the best of all are soaps of the high aromatic fatty acids higher than decoic acid; these soaps form insoluble calcium compounds, but other substances which form similar compounds injure the heart. Serum (but not the serum proteins) is beneficial; the same is true for serum lipoids, lecithin, and saponified serum lipoids. The loss of lipoids is the chief cause of the hypodynamic state; and the function of calcium is to cause an alteration in the colloidal state of the lipoids at the cell-surface. W. D. H.

The Mucin of the Stomach. J. López-Suárez (*Biochem. Zeitsch.*, 1913, **56**, 167—175).—By extraction of mucin from pig's stomach with 2% potassium hydroxide solution, and addition of acetic acid to the extract, a product was obtained which contained purine bases and also lipoids. By repeated solution in alkali and reprecipitation, a substance free from purine bases could be obtained. This contained (after extraction with alcohol and ether), 53·8% carbon, 7·29% hydrogen, 16·30% nitrogen, 1·47% sulphur, and 4·45% phosphorus. Chondroitinsulphuric acid, prepared from the mucin by Kondo's method, contained 43·3% carbon, 5·47% hydrogen, 5·37% nitrogen, and 4·29% sulphur. The former product contains less oxygen and sulphur than a true mucin, and in other respects differs from it widely in chemical composition. The stomach mucin appears to be a mixture of proteins, in which the chondoprotein is largely replaced by a nucleoprotein.　　S. B. S.

Carbon Dioxide Formation in the Liver. Eduard Freise (*Biochem. Zeitsch.*, 1913, **54**, 474—502).—An apparatus is described for perfusing liver with blood, and for estimating the carbon dioxide formed in the process, for which purpose the blood is treated with a stream of oxygen, and the mixture of gases is then led through a special absorption apparatus containing barium hydroxide solution. By the artificial perfusion of livers of rabbits or dogs with the blood of calf or ox, 54·74—192·48 mg. of carbon dioxide were formed per minute by 1 kilo. of the organ. This amount could be increased up to 50% by the addition of various oxidisable substances, such as dextrose, pyruvic acid, glyceric acid, and lactic acid. The addition to the blood, on the other hand, of galactose, glyoxylic acid, glycollic acid, and acetic acid, exerted no such influence.　　S. B. S.

The Effect of Water Ingestion on the Fatty Changes of the Liver in Fasting Rabbits. M. R. Smirnow (*Amer. J. Physiol.*, 1913, **32**, 309—314).—Fasting causes in rabbits fatty infiltration of the liver; if water is given, however, this as a rule does not occur.　　W. D. H.

Formation of Sugar in the Frog's Liver. Ivar Bang (*Biochem. Zeitsch.*, 1913, **56**, 153—157).—A reply to the criticisms of Lesser (this vol., i, 931).　　S. B. S.

Glyoxalase. III. The Distribution of the Enzyme and its Relation to the Pancreas. Henry D. Dakin and Harold W. Dudley (*J. Biol. Chem.*, 1913, **15**, 463—474).—This enzyme converts α-ketonic aldehydes, such as methyl- and phenyl-glyoxals, into optically active lactic and mandelic acids. It is probably important in carbohydrate metabolism. It is found in all tissues except the pancreas, which tissue contains an anti-glyoxalase, that is very powerful, and thermolabile. The inhibiting action is not limited to glyoxalase derived from the same species. It is present in pancreatic juice, in commercial pancreatic preparations, and in

the dry state lasts indefinitely (eight years in one case). It is destroyed at 85°, and by digestion with weak hydrochloric acid. Weak alkali is less injurious. The inactivation it produces is a function of the time of action. Whether it is an enzyme or not is unsettled. It is not trypsin, lipase, or diastase. The pyloric caeca of the fish (considered to be homologous with the pancreas) contain no anti-glyoxalase. The blood and tissues of diabetic men and dogs contain less glyoxalase than the normal, but this conclusion demands further work.   W. D. H.

Influence of Pancreatic and Duodenal Extracts on the Glycosuria and Respiratory Metabolism of Depancreatised Dogs. JOHN R. MURLIN and B. KRAMER (*J. Biol. Chem.*, 1913, 15, 365—383).—The effect of injecting pancreatic extract by itself and when mixed with duodenal mucosa extract on the dextrose : nitrogen ratio in the urine of a depancreatised dog, was investigated. This ratio was increased in the day following the injection, but a slight fall followed in the hourly elimination shortly after the injection, which was followed by a compensatory increase. In one case, when the mixed extracts were injected, there was for a short interval a complete disappearance of sugar. A similar effect could be produced by making Ringer's solution as alkaline as the extracts, and a marked diminution of sugar output could also be caused temporarily by injection of 2% sodium carbonate solution. The effects of the extracts are to be explained possibly by the alteration of the acidity. It is also possible that pancreatic extracts alter the permeability of the kidneys. The extracts, within the time of maximal glycosuria, produced no effect on the respiratory quotient, and there is therefore no evidence that they increased the combustibility of sugar in the organism.   S. B. S.

The Production and Utilisation of Glycogen in Normal and Diabetic Animals. E. W. H. CRUICKSHANK (*J. Physiol.*, 1913, 47, 1—14).—After extirpation of the pancreas, the liver rapidly and almost completely loses its glycogen, and becomes loaded with fat. Minkowski's statement that feeding diabetic animals on lævulose produces glycogen-storage was not confirmed. The percentage of glycogen in heart muscle varies, but averages 0·5; it is increased by copious carbohydrate food, and lessened by a diet devoid of protein and carbohydrate. During great activity, the heart may use all its stored glycogen in a few hours. In pancreatic diabetes, the cardiac glycogen rises, and may be entirely consumed if great activity of the heart occurs, as, for instance, after adrenaline. After death, both normal and diabetic hearts contain a glycogeno-lytic enzyme, so that the glycogen rapidly disappears if the heart is kept warm after the incubation has ceased.   W. D. H.

Influence of Extirpation of the Pancreas on the Endo-cellular Activity of the Liver Diastase. I. ERNST J. LESSER (*Biochem. Z-itsch.*, 1913, 55, 355—356).—The extirpation of the pancreas from frogs causes changes in the organism in many

respects analogous to those produced by diabetes in the human subject. It was shown that whereas the post-mortem diminution of the liver glycogen in frogs with intact pancreas was 4·2% in three and a-half hours at 22°, that of the depancreatised animals was 15·5%. The difference is explained, as the result of the author's previous experiments (this vol., i, 1129), by the assumption that the inhibition of the diffusion of the diastase to the glycogen which exists in the intact frogs has been removed. The experiments were carried out by the method already described, care being taken to keep the livers as free from damage as possible after removal from the body.   S. B. S.

The Physiology of the Glands. XIV. The Function of the Spleen as an Organ of Protein Metabolism, and the Compensatory Processes after Splenectomy. LEON ASHER and HANS SOLLBERGER (*Biochem. Zeitsch.*, 1913, 55, 13—44).—Immediately after the extirpation of the spleen of a normal rabbit on an iron-rich diet, there is an increase in the hæmoglobin content, and the number of red corpuscles in the blood, which may be explained by diminution of hæmolysis in the absence of the spleen and possibly an increased functioning capacity of the bone-marrow. The withdrawal of a small quantity of blood from the splenectomised animal causes a smaller diminution of hæmoglobin and of blood corpuscles than in a normal animal, and in the former case the blood much more rapidly attains its normal, or even hypernormal, condition. This fact indicates increased functional capacity of the bone-marrow when the spleen is absent. A similar difference between the splenectomised and normal animals was observed when larger amounts of blood were withdrawn. A difference was also observed when the organism was deprived of oxygen by the administration of hydrocyanic acid administered subcutaneously in the form of *aqua amygdalarum amarum.* In the splenectomised animal the treatment resulted ·again in a smaller diminution of hæmoglobin and red corpuscles, and the reversion to the normal condition of the blood was also more rapid. The extirpation of the thyroids had no specific effect on the hæmoglobin formation in splenectomised animals, or on the effect of hydrocyanic acid on either the splenectomised or normal animals. The general conclusion from the experiments seems to be that on iron-rich diet the functions of the bone-marrow are increased in the absence of the spleen.
                                                S. B. S.

The Intra-renal Resorption of Chlorides in Different Conditions of the Kidney. RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, 157, 487—490. Compare *ibid.*, 1913, 156, 1958).—The resorption of chlorides by the kidneys, on exercising a contra-pressure by means of a canula inserted in the urether and connected to a vessel of water, is reduced to an almost negligible quantity if the water is replaced by a solution of quinine sulphate (1 in 250), or by solutions of numerous toxic substances, or by the use of water after previous section of the splanchnic nerve.
                                                W. G.

The Iodine Content of Fish Thyroids. ALEXANDER T. CAMERON (*Biochem. J.*, 1913, **7**, 466—470).—Although iodine has been found in many marine animals, no estimations have hitherto been made for the thyroids of fishes; the percentage in the thyroids of the ray and dogfish averages 1·16%. The highest figure previously obtained in mammals is 0·7 in the dog.   W. D. H.

The Carbon Dioxide Formation in Surviving Perfused Muscles. HERBERT ELIAS (*Biochem. Zeitsch.*, 1913, **55**, 153—168).— The hinder extremities of dogs were employed, and they were perfused with ox-blood by the apparatus described by Freise (this vol., i, 1267), whose method of estimating the amount of carbon dioxide formed, was employed. At rest, the muscles produce about 7 mg. of carbon dioxide per kilo. per minute, which quantity can be largely increased by tetanisation (up to fifteen times the amount).   S. B. S.

Glycolysis by Muscular Tissue. ALFRED GIGON and MAX MASSINI (*Biochem. Zeitsch.*, 1913, **55**, 189—194).—This work was undertaken with the object of reinvestigating the statement of Cohnheim, that sugar is destroyed by incubation with muscular tissue, only in presence of pancreatic substances, as this result has not been confirmed by subsequent observers. A method is described for removal from rabbits of muscular tissue under aseptic conditions. This was disintegrated by freezing with solid carbon dioxide in sterile leather bags and breaking up in the frozen state. It was found that muscular tissue alone, in the absence of pancreas or liver powder, was capable of destroying 85% of the added sugar within twenty-four hours. Salts appear to be necessary for the process, and the best results were obtained when the sugar was incubated with the tissue in Ringer's fluid in the presence of small quantities of sodium hydrogen carbonate. The addition of pancreas, liver, or suprarenal tissue did not appear to increase the amount of sugar destruction.   S. B. S.

Pigments. A New Method for the Preparation and a Comparison of the Various Hair Pigments. HUGO FASAL (*Biochem. Zeitsch.*, 1913, **55**, 393—401).—The method of preparation consisted in treating the hair or other keratinous material with twenty-five times the weight of cold saturated potassium hydroxide solution. The protein is thereby dissolved, and the pigment separates; it is purified by dissolving in hot 5% potassium hydroxide solution, in which it dissolves; the solution is filtered off from any undissolved inorganic matter when cold, and the pigment is then precipitated by addition of acid. The examination of hair of different colours indicated that the difference in colour is due to the differences in the amount of pigment, and dark hair which has been deprived of its colour by hydrogen peroxide is nearly free from pigment. White hair contains but very small quantities. The ratio of the amount of pigment in the most strongly coloured hair to that in the least coloured was found to be 30 : 1.   S. B. S.

Investigations on Cell Proteins by means of Addition of Formalin. HUGO WIENER (*Biochem. Zeitsch.*, 1913, **56**, 122—152).— The cells of organs of different animals contain soluble proteins, which can be divided into two classes. The chief difference between these is that one class is precipitated by formalin, whereas the other is not. The proteins, which are precipitable by formalin, are considered by the author to belong to the tissue proteins. On washing out the organs in situ, the soluble proteins do not go entirely into the saline solution, owing, apparently, to the semipermeability of the cell-walls. They are only extractible when the cells are destroyed, either by grinding to a paste, or better still, by drying to a powder by Wiechowski's method. If, however, formalin (2%) is added to the saline perfusion liquid, the cell walls are injured, and the semipermeability is destroyed. The soluble proteins can ·then be readily washed out. In this case, only the soluble proteins which are not precipitated by formalin are obtained. By long perfusion with saline, the walls are also slightly injured, and a small amount of soluble proteins will pass out, so that it is difficult to obtain a perfusion liquid protein-free. Formalin can be used to separate three kinds of protein in the cell, namely, the insoluble proteins, the soluble proteins precipitable by formalin, and the soluble proteins not precipitable by formalin. From a comparison of the amounts obtained from the livers of fed and fasting dogs (the latter, for example, contains small quantities of soluble protein not precipitable by formalin), the conclusion is drawn that the three classes represent stages in the conversion of the protein of the food into the protein of the organ; there is, that is to say, no hard and fast line between the fixed and circulating proteins.

S. B. S.

The Distribution of a Keto-reductase in Tissues. L. VON LAGERMARK (*Biochem. Zeitsch.*, 1913, **55**, 458—462).—Friedmann and Maase have shown that the liver contains a ferment capable of reducing acetoacetic acid to *l*-β-hydroxybutyric acid. It is now shown that this ferment exists also in the muscles and in the kidneys, but not in blood, lungs, the pancreas, or the spleen. The organs investigated were removed from fasting dogs. S. B. S.

Changes in the Reaction of Growing Organisms to Narcotics. HORACE M. VERNON (*J. Physiol.*, 1913, **47**, 15—29).— As tadpoles grow, the narcotising concentration of methyl and ethyl alcohol falls, but that of propyl alcohol remains constant, and of higher alcohols increases; the quotients between the narcotising concentration of successive alcohols vary. The effect of ethyl acetate, propionate, butyrate, and valerate does not alter with age; that of three ketones diminished during growth. The fatal concentrations of monohydric alcohols vary greatly with age. These changes are attributed in most part to changes in the composition of cell-lipoids. W. D. H.

The Function of the Ferments in the Animal Body after Introduction of Killed Tubercle Bacilli. Nina Kotschnev (*Biochem. Zeitsch.*, 1913, 55, 481—494).—The introduction of killed tubercle bacilli into rabbits and guinea-pigs caused a diminution of the lipoclastic properties of the serum and organs, and an increase in their antitrypsin and nuclease content. The catalase of the serum and organs was diminished in energy in the case of guinea-pigs only. There was a slight diminution of the amylase and diastase content of serum and organs.   S. B. S.

The Presence of Adenase in the Human Body. Esmond R. Long (*J. Biol. Chem.*, 1913, 15, 449—462).—Aderase could not be found in human adult liver, the placenta or fœtal liver, brain, bone, thymus, stomach, intestine, pancreas, lungs, and spleen. It is, however, present somewhere in the fœtus, for if the entire fœtal material is mixed with adenine, hypoxanthine is formed. Hypoxanthine is always formed in the autolysis of human tissues, and in the absence of adenase is probably due to the action of adenosine deamidase and inosine hydrolase.   W. D. H.

The Tyrosineoxydase, Polyphenoloxydase, and Oxydones of Insects. Fred. Battelli and Lina Stern (*Biochem. Zeitsch.*, 1913, 56, 59—77).—All the above ferments are contained in the insects investigated. The fully developed insect contains less polyphenol oxydase than the larva and chrysalis of the same species. p-Phenylenediamine is oxidised less energetically than quinol and pyrogallol by pulverised insects, which is in marked contrast to the action of vertebrate tissue. There is no parallelism between the polyphenoloxydase content of insects and the respiratory exchange of the living insect. As a rule, those insects which have the largest content in polyphenoloxydase have also the largest amount of tyrosineoxydase. Both ferments can be obtained in powder form by treatment of an insect paste with acetone or alcohol. Tyrosine is oxidised with evolution of carbon dioxide. Insects contain no uricoxydase. There is no alcohol oxydase in silk-worms. Insects contain a succino-oxydone, but the oxidation of succinic acid is much weaker than that of the polyphenols and tyrosine. This oxidation is also weaker in the case of insects than in the case of muscular or liver tissue of mammals. There is a rough parallelism between the oxidation of succinic acid by pulverised insects and the oxidation energy of the living animals. Citric acid is not oxidised by insect paste, and the intensity of the oxidation by pulverised insects is uninfluenced by the addition of sodium acetate, sodium lactate, or dextrose.   S. B. S.

Physical Properties and Chemical Composition of Frog's Urine. Shozo Toda and Katsuta Taguchi (*Zeitsch. physiol. Chem.*, 1913, 87, 371—378).—The reaction of frog's urine is usually feebly acid to litmus paper; D 1·0009 to 1·0018; $\Delta = 0·106$. The electrical conductivity in reciprocal ohms is $0·78 \cdot 10^{-3}$. In summer frogs, the urine contains 0·193 of organic and 0·053 of inorganic con-

stituents %; of the latter 0 0467 are salts soluble in water. There
is a relative large amount of phosphoric acid and sodium. The
proportion of sodium to potassium is 1·7 : 1.   W. D. H.

The Chemistry of Cancerous Tumours. B. WOLTER (*Biochem.
Zeitsch.*, 1913, **55**, 260—265).—Analyses of the total phosphorus and
its distribution as inorganic, phosphatide and protein phosphorus
from a liver sarcoma, from the surrounding liver tissue, and from
the tissue of normal liver, are given. The most marked difference
in the analyses of the tumour and other tissues was the somewhat
smaller percentage (both relative and absolute) of the phosphatide
phosphorus in the former. The amount of cholesterol in the
tumour was 0·25% of the fresh tissue.   S. B. S.

Disturbances in the Protein Metabolism in Cancer. (The
Excretion of Thiocyanates.) PAUL SAXL (*Biochem. Zeitsch.*,
1913, **55**, 224—244).—It has been found that the urine in cases
of cancer generally contains excess of nitrogen, but the amount of
urea is less than the normal, whereas the quantities of oxyproteic
acid and ammonia are greater. The urine of cancer patients is
also characterised by containing a certain amount of sulphur in a
form in which it is readily oxidised to sulphuric acid. These
results suggest the presence of thiocyanates, due to hydrogen
cyanide, split from proteins, and not completely oxidised. Similar
urines were obtained from normal individuals after administration
of thiocyanates. It is now directly shown that, in the majority
of cancer cases, the urine contains abnormally large amounts of
thiocyanate, which is the source of the easily oxidised sulphur.
Other pathological urines also yield abnormally large amounts, but
not to quite the same extent as those from cancer patients. The
thiocyanate was estimated by precipitation with silver nitrate in
acid solution; the silver salt was then dissolved in sodium hydrogen
carbonate, and treated with excess of $N/10$-iodine solution and
potassium iodide. After four hours, hydrochloric acid is added,
and the excess of iodine estimated by titration. The amount of
thiocyanate can be calculated from the equation :

$$CNSK + 3I_2 + 4H_2O = H_2SO_4 + 5HI + KI + HCN.$$
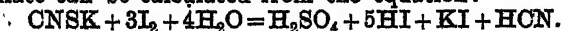
S. B. S.

Protozoan Protoplasm as an Indicator of Pathological
Change. II. In Carcinoma. FRANK P. UNDERHILL and LORANDE
LOSS WOODRUFF (*J. Biol. Chem.*, 1913, **15**, 401—414).—Extracts of
breast cancer depress the division rate of *Paramœcium*, and kill
the protozoon. Extracts of normal mammary tissue do not possess
this property. Weak concentrations of the abnormal extracts may
stimulate the *Paramœcium*.   W. D. H.

The Tryptophan Content of Normal and Pathological
Cutaneous Tissues, and of Malignant Tumours. HUGO FASAL
(*Biochem. Zeitsch.*, 1913, **55**, 88—95).—By means of the author's
colorimetric method, the tryptophan content in various normal

and pathological tissues was estimated. The epidermis is relatively rich in this substance, as are certain tumours, such as carcinoma of the liver. Mammary tumours, on the other hand, do not contain a trace.   S. B. S.

A Case of Pentosuria. PHŒBUS A. LEVENE and FREDERICK B. LAFORGE (*J. Biol. Chem.*, 1913, **15**, 481—486).—Neuberg states that the usual pentose in cases of pentosuria is *dl*-arabinose. Elliott and Raper described a case in which it was probably ribose. In the present case much of the pentose was lost in the methods adopted for its separation, and the identification of the sugar was not complete, but it was probably *l*-ribose.   W. D. H.

The Origin of the Sugar Secreted in Phloridzin Glycosuria. RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, **157**, 530—532. Compare A., 1904, ii, 753).—The authors quote experiments which, they maintain, contradict the generally accepted hypothesis that the sugar eliminated in phloridzin glycosuria comes from the renal cells. They consider that the point of attack of the phloridzin in the kidney is the vascular endothelium.   W. G.

The Production of Fever. MAX CLOETTA and ERNST WASER (*Arch. expt. Path. Pharm.*, 1913, **73**, 436—456).—By subcutaneous and intravenous injection of the monomethyl derivative of alicyclic tetrahydro-β-naphthylamine, the body temperature is raised in a few minutes. This rise occurs in the region of the cerebral ventricles within twenty seconds, and in the fore-brain in about forty to sixty seconds; the intestinal temperature rises next, and finally that of the skin (which falls during the first half minute). If death occurs, the intestine and skin remain warm after the temperature falls in the central nervous system.   W. D. H.

Protozoan Protoplasm as an Indicator of Pathological Changes. I. In Nephritis. LORANDE LOSS WOODRUFF and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1913, **15**, 385—400).—Extracts of normal kidneys from well-fed and starving animals exert no effect on the division rate of *Paramœcium*; but extracts of nephritic kidneys depress it. This is not due to accumulation of tartrate which was given to induce nephritis. The experiments were made on rabbits.   W. D. H.

The Chemistry of the Leucocytozoon Syphilidis and of the Hirt's Protecting Cells. JAMES E. R. MCDONAGH and R. L. MACKENZIE WALLIS (*Biochem. J.*, 1913, **7**, 517—543).—Much of the work recorded relates to the properties of the colloidal dyes used for micro-chemically investigating the syphilis parasite. Basic stains are most suitable for work in vivo, and of these borax-methylene-blue is the best. The parasite has a lecithin-globulin envelope which stands out more clearly by adding dextrose to the stain. The varied affinity shown for methylene-violet and methylene-red is due to the prevalence of a substance which has

strong reducing properties (lecithin-globulin), and not to a change in the reaction. Details are given of the staining reactions of different parts of the parasite, but the whole subject is at present of subsidiary chemical interest.   W. D. H.

(Pharmacological) Action of Bromine Salts. E. BERNOULLI (*Arch. expt. Path. Pharm.*, 1913, 73, 355—397).—The theory of chlorine poverty is insufficient to explain the action of alkali bromides. For the neutralisation of the bromine action, the administration of chlorides is not necessary, but other salts (sodium sulphate and nitrate) act in the same way. Bromine salts cause changes in the colloidal material of the central nervous system. The bromine ions which take the place of chlorine ions alter the aggregation state of the cell-colloids, probably in the direction of greater swelling, and thus is produced a functional change in the nerve-cells.   W. D. H.

The Action of Leucocytes and Other Tissues on *dl*-Alanine. PHŒBUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem.*, 1913, 15, 475—480).—Leucocytes under aseptic conditions form *d*-lactic acid from hexoses, regardless of the configuration of the hexose. The conversion of amino-acids into hydroxy-acids is analogous to the change of methyl-glyoxal into lactic acid; thus, alanine is transformed into lactic acid through the stage of pyruvic acid. Dakin, Dudley and Ringer found in diabetic dogs fed on pyruvic acid that the yield of sugar was smaller than from either alanine or lactic acid. Hence in the present research the action of leucocytes was tested on various forms of alanine. The unexpected result obtained was that neither leucocytes nor kidney tissue had any effect at all on *dl*-alanine.   W. D. H.

The Behaviour of Pyruvic Acid in the Animal Body. II. GUSTAV EMBDEN and MAX OPPENHEIMER (*Biochem. Zeitsch.*, 1913, 55, 334—340. Compare A., 1912, ii, 1075).—As pyruvic acid is a possible intermediate product in the conversion of alanine into lactic acid, it was of interest to ascertain whether the latter acid could be obtained directly from the former in the animal body. It was found that this change could be accomplished when pyruvic acid was perfused through a glycogen-poor liver of a dog which had been starved for four days. It was obtained in the *d*-form.
                                                       S. B. S.

The Behaviour of Pyruvic Acid in the Animal Body. III. The Formation of Sugar and Lactic Acid from Pyruvic Acid. PAUL MAYER (*Biochem. Zeitsch.*, 1913, 55, 1—3).—The author recapitulates his former results, which indicate that pyruvic acid, on administration to rabits and dogs, causes hyperglycæmia and glycosuria, but that on administration to animals treated with phloridzin, it causes a diminution of the sugar and nitrogen output in the urine, owing apparently to a toxic action on the kidneys. He is not able to explain the difference between his results and those obtained by A. J. Ringer and by Dakin and Janney (this vol.,

i, 937), but rejects the explanation offered by the former. Animals to which pyruvic acid has been administered excrete in the urine both dl- and d-lactic acids.   S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XV. The Behaviour of Benzaldehyde in the Animal Body. ERNST FRIEDMANN and WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, 55, 425—431).—After administration of benzaldehyde to dogs, only hippuric acid and small quantities of benzoic acid, but no cinnamic acid, could be isolated in the urine. The cinnamic acid found by Dakin after administration of phenylpropionic and phenylvaleric acid must be due therefore to degradation, and not to synthesis by condensation of an aldehyde with acetic acid.   S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XVI. Behaviour of a-Phenylbutyric Acid in the Animal Body. ERNST FRIEDMANN and WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, 55, 432—435).—As γ-phenylbutyric acid undergoes in the animal body oxidation in the β-position to yield a keto-acid and finally phenyl-acetic acid, it was of interest to ascertain how the a-acid $CH_3 \cdot CH_2 \cdot CHPh \cdot CO_2H$ would behave. If oxidation were to take place in the β-position, phenylacetic and acetic acid should be expected as final products, according to the equations given by the authors. As a matter of fact, only unchanged a-phenylbutyric acid, and a neutral substance, which was not further investigated, could be isolated in the urine of dogs, to which this substance had been administered.   S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XVII. Formation of Acetoacetic Acid from Acetic Acid in the Perfusion through the Liver. ERNST FRIEDMANN (*Biochem. Zeitsch.*, 1913, 55, 436—442).—Adam Loeb has shown that the addition of sodium acetate to the blood perfused through the surviving liver of a dog causes a marked increase in the amount of acetoacetic acid formed. This is in contrast to the author's own results, where no such increase was found. It is now shown that this increase only results when the liver is poor in glycogen, as, for example, in the livers of animals which have been starved and tetanised by strychnine. In this case increase of acetoacetic acid only follows when acetate is added to the perfusing blood. Such an addition causes no increase when the livers used for experiment are rich in glycogen and taken from a well-fed animal. The mechanism of the formation of acetoacetic acid from acetic acid is discussed, and it is suggested that acetaldehyde is an intermediate product, which condenses with acetic acid to form crotonic acid, from which, by addition of water and oxidation, acetoacetic acid is formed. It is further suggested that in presence of carbo-hydrates, acetic acid is condensed in some other way. From the fact that acetoacetic acid is only formed from fatty acids with an even number of carbon atoms, the conclusion is drawn that acids do not always form β-keto-acids as intermediary oxidation products,

as in this case acetic acid should always be formed, and this is, as the experiment shows, an acetoacetic acid former. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XVIII. Behaviour of Glycollic and Glyoxylic Acids in Perfusion through the Liver. JUNICHI MOCHIZUKI (*Biochem. Zeitsch.*, 1913, **55**, 443—445).—Friedmann has suggested (see preceding communication) that acetoacetic acid is formed from acetic acid in perfusion experiments by condensation of the latter with acetaldehyde to yield crotonic acid as an intermediate product. It follows, if this suggestion is correct, that no acetoacetic acid should be formed if the methyl group of acetic acid should have a hydrogen replaced by hydroxyl. As a matter of fact, it was found that neither from glycollic nor glyoxylic acid is acetoacetic acid formed.

S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XIX. Acetoacetic Acid Formation in the Perfusion of Livers Rich in Glycogen. JUNICHI MOCHIZUKI (*Biochem. Zeitsch.*, 1913, **55**, 446—449).—It has been shown by Friedmann (this vol., i, 1276) that acetoacetic acid is formed from acetic acid only when perfused through livers poor in glycogen. It is now shown that butyric acid, β-hydroxybutyric acid, crotonic acid, and *iso*valeric acid yield acetoacetic acid when perfused through livers rich in glycogen, whence the conclusion is drawn that acetic acid is not an intermediary product of reaction. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XX. Conversion of Crotonic Acid into *l*-β-Hydroxybutyric Acid by Liver Pulp. ERNST FRIEDMANN and C. MAASE (*Biochem. Zeitsch.*, 1913, **55**, 450—457).—Crotonic acid is converted into *l*-β-hydroxybutyric acid in the presence of liver pulp obtained from a fasting dog. Carbon dioxide inhibits the reaction. S. B. S.

The Fixation of the Digitalis Substances in the Animal Organism, Considered more Especially with Reference to their Behaviour in the Blood. ERNST OPPENHEIMER (*Biochem. Zeitsch.*, 1913, **55**, 134—152).—Various investigators have failed to detect these substances in the tissues after injection into animals, and researches were undertaken to ascertain the cause of this failure. It was found that the slightly soluble digitoxin is only slowly precipitated from its alcoholic solution. The solutions of both amorphous, slightly insoluble, digitalis glucosides are dialysable, and behave in this respect like the easily soluble crystalline glucosides, strophanthin and antiarin. As precipitation in the blood-stream does not account for the apparent absence of the substances in the blood-stream, the effect on their toxic action due to the admixture with serum was determined, Straub's method for estimating the toxicity (action on frog's heart) being employed. It was found that serum could diminish or destroy the toxicity of the following substances: digitoxin, gitalin, digitalin, oleandrin,

saponin, and methyl-violet. It increased the toxicity, on the other hand, of strophanthin and antiarin. This action of the serum cannot be replaced by either cholesterol, egg-white, or lecithin in Ringer's fluid. These experiments indicate that the failure to detect digitalis alkaloids after injection into the organism is not due to its fixation by cells of the tissues.   S. B. S.

Action of Enzymes on Racemised Proteins and their Fate in the Animal Body. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, 15, 271—276).—" Racemised" casein and caseose are resistant to the action of pepsin, trypsin, and erepsin. On feeding the substances to a dog *per os*, they were excreted unchanged in the fæces, no absorption having taken place in the intestine. It appears as if this organ can take up only comparatively simple substances. Racemised caseose, when administered subcutaneously to a dog, produced no symptoms, and was excreted unchanged in the urine. "Racemised" casein remained unchanged in the presence of bacteria, but the caseose was slowly attacked, yielding indole and other products.   S. B. S.

The Behaviour of Iodoprotein in the Organism. JULIUS WOHLGEMUTH and BRUNO REWALD (*Biochem. Zeitsch.*, 1913, 55, 7—12).—The preparation of an iodine derivative from coagulated blood by means of an alcoholic solution of iodine is described, which contains about 15% of iodine and 0·25% of iron. Preliminary therapeutic experiments indicate that this preparation is well tolerated in relatively large doses by rabbits, dogs, and man. In the experiments on rabbits, it was shown that the iron accumulates in the liver. The preparation is readily absorbed, and about 70% of the iodine is excreted in the urine between the third and forty-eighth hours after administration. Little or no iodine is found in the fæces.   S. B. S.

Degradation of the Naphthalene Ring in the Animal Body. ERNST FRIEDMANN and WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, 55, 463—476).—β-Naphthylalanine and β-naphthylpyruvic acid are degraded in the organism to benzoic acid. In order to study the influence of the side-chains on the degradation of the naphthalene nucleus, the degradation of the following products was studied: β-naphthoic acid, β-naphthylacetic acid, and (in greater detail) β-naphthylpyruvic acid. The former results with the last-named were confirmed, in that in the urine of dogs to which it had been administered an excess of hippuric acid was found. This did not happen in the case of either the naphthoic or naphthylacetic acids. The pyruvic acid derivative, however, yielded hippuric acid only when administered *per os*, but not when subcutaneously applied, and the conversion into benzoic acid is therefore possibly a putrefactive process in the intestines. After administration of β-naphthoic acid, in addition to unchanged product, naphthuric acid was found in the urine both after administration *per os* and after injection under the skin. A conjugation with glycine had

therefore taken place. After administration of β-naphthylacetic acid, a considerable amount of unchanged product was found in the urine. The fate of the remainder is still unknown. S. B. S.

The Influence of the Subsidiary Alkaloids of Opium on the Action of Morphine. RICHARD MEISSNER (*Biochem. Zeitsch.*, 1913, **54**, 395—429).—The experiments were carried out with a view to demonstrate the potentialising capacity of other alkaloids on the pharmacological action of morphine, as shown by Straub. The action on the respiratory centre of rabbits, the narcotic action on cats, and the action on the isolated intestine of rabbits were investigated. A larger diminution in the respiratory volume was produced by narcophine, but apart from this, no essential difference was found in the actions of narcophine, pantopone, or laudenone. The investigations appear to negative the conception of a potentialising action of narcotine on morphine. Nevertheless, the results must be accepted with some caution, in view of some quoted experiments of Zehbe on the action of various preparations on the human intestine. S. B. S.

Degradation of Phenylalanine in the Animal Organism. GUSTAV EMBDEN and KARL BALDES (*Biochem. Zeitsch*, 1913, **55**, 301—322).—The general theory as to the relationship between the combustibility of amino-acids in the normal organism, their convertibility into homogentisic acid in alcaptonuric individuals, and their conversion into acetoacetic acid when perfused through the liver is discussed. Phenylpyruvic acid, a conceivable first oxidation product of phenylalanine, both of which substances are burnt up in the organism and converted into homogentisic acid in alcaptonuric cases, might be expected, like substances generally with this behaviour, to be convertible into acetoacetic acid by perfusion through the liver, especially as phenyl-lactic acid, and the keto-acid corresponding with tyrosine, undergo this change. This was found, however, not to be the case; on the contrary, phenylpyruvic acid even inhibits the acetoacetic acid formation from phenylalanine, tyrosine, leucine, and p-hydroxyphenylpyruvic acid when these are perfused in its presence. On the other hand, it does not inhibit acetoacetic acid formation from *iso*valeric or n-hexoic acids, and does not therefore act as a general inhibitor of oxidation processes in the liver. It possibly combines with the side-chains in the cell to which the amino-acids are normally attached when converted into acetoacetic acid. These facts suggest that phenylpyruvic acid is not the first oxidation product of phenylalanine, but oxidation takes place, probably, first in the benzene nucleus. It was found, in fact, that dl-phenylalanine, when perfused through the liver, gives rise to the normal l-tyrosine. From this, p-hydroxyphenylpyruvic acid could be formed, which is an acetoacetic acid former. It is suggested that when phenylpyruvic acid is burnt in the organism, it is converted first into phenylalanine, as it is known that the change of amino- into keto-acids in the body is a reversible one. S. B. S.

The Relations between Constitution and [Physiological] Action in Alicyclic Tetrahydro-β-naphthylamine and its Derivatives. Max Cloetta and Ernst Waser(*Arch. expt. Path. Pharm.*, 1913, 73, 398—435).—From the substance mentioned, optically active *d*- and *l*-bases can be isolated, which resemble the racemic base in their action. From the latter a series of salts can be prepared with differing dissociation capacities, but no relation was found between this property and toxicity. The monomethyl derivative, like the original base, dilates the pupil, and raises body temperature and blood-pressure; the corresponding monoethyl compound acts in the same way, but is more toxic. If, however, the nitrogen is replaced by an acid residue (acetyl, formyl), the actions are reversed, the pupil is narrowed, and body temperature and blood-pressure fall. If an acid and alkyl group are both introduced there is a double action; for instance, in the frog, myosis is produced by the acid group, and in the rabbit, mydriasis by the alkyl group. In the case of derivatives that raise the blood-pressure, a second injection is not effective in the same way.   W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Fermentation of Pyruvic Acid by Bacteria. László Karczag and L. Móczár (*Biochem. Zeitsch.*, 1913, 55, 79–87).—The bacteria which are capable of fermenting dextrose with evolution of gas are also able to ferment pyruvic acid. Amongst such bacteria are *B. coli*, *B. paratyphi-B.*, and Gaertner's bacillus. The gas evolution with bacteria follows more rapidly than with yeast, but there is a marked difference between the two classes of fermentations, for whereas with yeast the gas evolved is carbon dioxide, the pyruvic acid yielding this gas and formaldehyde, the gas evolved by bacteria consists for the most part of hydrogen.   S. B. S.

Formation of Hydrogen Cyanide from Proteins. H. W. Emerson, Hamilton P. Cady, and E. H. S. Bailey (*J. Biol. Chem.*, 1913, 15, 415—418).—Certain micro-organisms (*B. pyocyaneus*) evolve hydrogen cyanide when grown on protein media, especially if the medium is slightly acid to litmus and phenolphthalein. This is absent when free mineral acid is present.   W. D. H.

Formation of Hydrogen Cyanide from Proteins. B. J. Clawson and C. C. Young, (*J. Biol. Chem.*, 1913, 15, 419—422).—*B. pyocyaneus, B. fluorescens, B. violaceus*, and other bacteria the nature of which is still uncertain, produce hydrogen cyanide from protein material.   W. D. H.

Chemistry of Bacteria. Sakae Tamura (*Zeitsch. physiol. Chem.*, 1913, 87, 85—114).—Chemical investigations were made on large

quantities of the cells of *Bacillus tuberculosis* and *Mycobacterium lacticola perrugosum.* Extraction with ether failed to give any phosphatides, but treatment with warm alcohol showed the presence of a diaminomonophosphatide in each species of bacteria. Both cultures were found to contain an alcohol ($C_{29}H_{56}O$), for which the name *mycol* is suggested. This alcohol is present in the bacterial cell partly as an ester of a higher fatty acid, and it is to the alcohol or its ester that the acid- and alkali-resistance and gram-positiveness of the organisms are due. Adenine and hypoxanthine were present in each case, in addition to arginine, histidine, lysine, phenylalanine, proline, valine, tyrosine, and tryptophan. Bacterio-proteins are characterised by a high phenylalanine content.

H. B. H.

Fermentation of Cellulose by Thermophilic Bacteria. HANS PRINGSHEIM (*Centr. Bakt. Par.*, 1913, ii, 38, 513—516).—Impure cultures of anaerobic, thermophilic, cellulose-decomposing bacteria were obtained from soil and horse manure. By means of a special apparatus the cultures were maintained at 55—60°, and samples of the decomposition gases were withdrawn from time to time. These were found to consist of 22—49% carbon dioxide, and the residue in all cases proved to be hydrogen.

Examination of the residual liquid cultures showed the presence of formic and acetic acids, but no butyric acid. This is significant, as the latter is the chief product of anaerobic cellulose decomposition at normal temperatures. Three grams of cellulose led to the production of 0·2125 gram of formic acid, 1·15 gram of acetic acid, a trace of lactic acid, and a mixture of carbon dioxide and hydrogen in the above proportions.

H. B. H.

The Enrichment of the Invertase Content of Living Yeasts. LEOPOLD LICHTWITZ (*Biochem. Zeitsch.*, 1913, 56, 160—162).—The author replies to certain criticisms of Meisenheimer, Gambarjan, and Semper (this vol., i, 1139), who found that the invertase con-tent of yeast increases when the organism is kept in sugar solution. This is the direct contrary of what was found by the author. He calls attention to the fact, however, that yeast sown in large quantities in sugar solution, as was done by Meisenheimer and his collaborators, does not increase; on the contrary, it probably autolyses. This did not happen in the author's own experiments; hence, probably, the difference in the results.

S. B. S.

Catalysts of Alcoholic Fermentation. HANS VON EULER (*Zeitsch. physiol. Chem.*, 1913, 87, 142—144).—Earlier work has shown that the rapidity of fermentation by living yeasts is accelerated by the addition of alkali salts of organic and especially fatty acids, and dried yeast or yeast juice is not affected in a similar manner. Of the two possible interpretations of the results, particular attention has been paid to that which assumes that the activation is not directly connected with enzymes in the yeast cell, and experiments have been made to determine an alteration

of the protoplasmic layer of the cell or of the cell wall generally by the salts, with adsorption and an alteration of surface tension.

Preliminary experiments with sodium and ammonium salts of the acids having given negative results, an attempt was made to determine the action of various dye salts on the living cell. According to their behaviour towards the yeast cell, it was possible to divide the dye salts into three classes, namely, those without action on the cell, those which are clearly adsorbed, and others the entrance of which into the cell depends on the fermentative activity of the latter. These phenomena and the part played by an alteration of the surface tension are being further investigated.

<div align="right">H. B. H.</div>

Influence of Certain Inorganic Salts, particularly Stannous Chloride and Bismuth Subnitrate, on Fermentation. GILBERT GIMEL (*Bull. Assoc. chim. Sucr. Dist.*, 1913, 31, 128—129).—Results of further experiments confirm those obtained previously by the author (A., 1909, ii, 171). The activity of various yeasts in sweet worts is increased when the latter contain from 50 to 100 mg. of stannous chloride per litre. Bismuth subnitrate is soluble in acid liquids, such as musts, etc., and has a decided influence on the fermentation; it appears to inhibit acetic fermentation. The use of pure yeast cultures and different conditions of fermentation are probably the reason of the opposite opinion arrived at by Pozzi-Escot (this vol., i, 1139).

<div align="right">W. P. S.</div>

Protein Degradation in Yeast. I. The Influence of Sugar Fermentation on the Protein Degradation of Yeast. W. ZALESKI and W. SCHATALOV (*Biochem. Zeitsch.*, 1913, 55, 63—71).— Various views have been expressed to explain the fact that proteolysis is less in yeast that has been used for sugar fermentation than in unused yeast, the Ivanov has stated that acetaldehyde is the fermentation product which is responsible for the antiproteolytic action. This statement the authors have been unable to confirm, for they find that an appreciable inhibition of yeast autolysis only takes place in concentrations of this aldehyde which are far higher than those found in fermentation liquors. The same is also true for furfuraldehyde and for formaldehyde, which latter, however, has a much stronger inhibitory action than acetaldehyde. Although the distillates from fermentations possess antiproteolytic properties, the actual antiproteolytic substance has not been isolated. The conditions of nutrition of the yeast exert some action on the subsequent proteolysis. The addition of amino-acids to yeasts increases the autolytic degradation of their proteins; it cannot be claimed, however, that they antagonise the antiproteolytic properties of the fermentation products.

<div align="right">S. B. S.</div>

Biochemical Conversion of Betaine into Glycollic Acid. FELIX EHRLICH and FRITZ LANGE (*B.r.*, 1913, 46, 2746—2752).—In the course of their experiments on the behaviour of amino-acids towards micro-organisms, the authors have examined betaine, which is remarkably stable, not only to concentrated sulphuric acid or

aqua regia at high temperatures, but also during passage through the bodies of most animals except the ruminants. They find that betaine is not assimilated by brewers' and distillers' yeasts or by various kinds of *Saccharomyces*, but is extensively degraded by *Willia anomala, Pichia farinosa, Pichia membranefaciens*, and other yeasts rich in oxydases; also many moulds, such as *Penicillium, Aspergillus, Monilia, Oidium*, and *Dematium*, are able to employ betaine for the formation of their albumin. In most cases characteristic degradation products of betaine cannot be isolated, partly because the decomposition is too extensive, partly owing to the difficulty of separating the decomposition products of the sugar added as a source of carbon. In experiments on solutions containing betaine, nutrient salts, and ethyl alcohol as a source of carbon, the authors find that after the addition of a pure culture of *Willia anomala* and keeping for eight weeks, glycollic acid is present in quantity sufficient for isolation; the amount is small, because the acid is an intermediate, not the final, product of the assimilation of the betaine. This is proved by the fact that *Willia anomala* grows extensively in a solution containing nutrient salts, and glycollic acid and carbamide as the only sources of carbon, the glycollic acid disappearing completely after four months; in a similar experiment, in which carbamide is the only source of carbon, growth of the yeast cannot be detected.

In the preceding experiments with betaine, not a trace of trimethylamine can be detected. Probably it is converted into methyl alcohol and ammonia, the latter, which also cannot be detected, being utilised by the organism in the formation of albumin.

In conclusion, the authors reply to Stoltzenberg (this vol., i, 345; compare also Ehrlich, A., 1912, i, 835; Stoltzenberg, *ibid.*, i, 680) concerning the isolation of betaine from molasses residue.

C. S.

Protein Synthesis in Plants. I. Protein Synthesis in the Bulbs of Allium cepa. W. ZALESKI and W. SHATKIN (*Biochem. Zeitsch.*, 1913, 55, 72—78).—Experiments confirm a former statement of Zaleski, that the proteins increase in quantity in the injured bulbs when left in a moist atmosphere or in intact bulbs when allowed to grow in the dark. Estimations were of the total nitrogen, proteins, peptones, ammonia, acid amides, organic bases, and mono-amino-acids. It was found, as a result, that the proteins are formed at the expense of the monoamino-acids. The mono- and di-amino-acids and ammonia were also estimated in the various specimens after hydrolysis with acids. The results obtained indicate that the monoamino-acids pre-existing combine with the pre-existing proteins. There is no evidence that the acid amides, without further change, take any direct part in the protein synthesis. S. B. S.

The Inulin Metabolism of Cichorium intybus (Chicory). III. VIKTOR GRAFE and VALENTIN VOUK (*Biochem. Zeitsch.*, 1913, 56, 249—257. Compare A., 1912, ii, 977; this vol., i, 148).—It is shown

that by the freezing of the roots, the amount of inulin decreases, whereas the amount of reducing sugar increases; the amount of the latter returns to normal when the frozen roots are afterwards kept at normal temperature, whereas the amount of inulin remains unchanged. These results confirm the theory of Molisch, that the dissolved inulin acts as a "thermically active" protector against cold. The changes in the inulin and reducing sugar distribution in the roots which had wintered in a normal manner were also investigated. It was found that a hydrolysis of inulin takes place before new parts of the plants are visible; the reserve substances appear to be converted into building material, and this allows the further hydrolysis of the inulin reserves. A résumé of the results obtained by the authors up to the date of publication is also given.   S. B. S.

The Colorimetric Method for Determining Hydrocyanic Acid in Plants with Special Reference to Kafir Corn. C. K. FRANCIS and W. B. CONNELL (*J. Amer. Chem. Soc.*, 1913, 35, 1624—1628).—After examining the various methods for the estimation of small quantities of hydrocyanic acid, the authors decide in favour of a colorimetric process depending on the formation of ferric thiocyanate. This method indicates that Kafir corn contains minute quantities of combined hydrocyanic acid, the quantity apparently being greater in frost-bitten or stunted plants than in normal ones.

It is difficult to decide from the results whether the quantity of hydrocyanic present could prove fatal to an animal fed with this material.   D. F. T.

Antitoxic Action of Chloral Hydrate on Copper Sulphate for Pisum sativum. R. P. HIBBARD (*Centr. Bakt. Par.*, 1913, ii, 38, 302—308).—Water culture experiments in which garden peas were supplied with solutions of copper sulphate in concentrations varying from $M3 \times 10^{-4}$ to $M2\cdot5 \times 10^{-6}$, and with chloral hydrate, $M/165\cdot5$ to $M/16,550$, both together and separately. After forty-eight hours the roots of the plants were measured. Whilst in the single solutions growth was very slight, when both substances were supplied simultaneously the growth was distinctly better, especially when both substances are present in about equal amounts. The action of chloral hydrate in diminishing the toxicity of copper sulphate is similar, although less marked, to the influence of calcium over magnesium salts.

Several explanations are suggested, the most important of which is perhaps connected with the extent of ionisation which may be retarded when both substances are present. Or, changes may be brought about in the plasma membrane which will modify the permeability of the limiting layer. Then, again, the effect may be the result of changes in the cell itself.   N. H. J. M.

Organic Chemistry.

Separation of Mixtures of a Saturated with an Unsaturated Hydrocarbon by means of Permanganate. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1423—1429).—Attempts to determine the proportions of the constituents of mixtures of (1) *cyclo*hexane and *cyclo*hexene, and (2) *n*-hexane and hexylene by oxidising the unsaturated hydrocarbon by means of permanganate were unsuccessful, owing to the saturated constituent reacting to some extent with the oxidising agent.

A similar method was then applied to analogous mixtures of gaseous hydrocarbons. For this purpose a special gas pipette was devised which permits the gaseous mixture to be passed repeatedly in small bubbles through the reagent, and in which the latter does not come into contact with mercury. After the reaction with saturated permanganate solution, the excess of oxidising agent was destroyed by means of saturated bisulphite solution, both this and the permanganate solution having been previously saturated with the saturated constituent of the gaseous mixture. With various mixtures of propane and ethylene, propane and propylene, and *cyclo*propane and propylene, the greatest error in the volume of the gas remaining after treatment with permanganate was 0·27%.

The unsatisfactory results obtained by Kishner (this vol., i, 153) are largely explained by the fact that, in most cases, the reaction was completed at 100°, and hence under conditions which should lead to attack of the saturated hydrocarbon. T. H. P.

Investigations on Polymerisation. I. Diethylene Hydrocarbons. SERGEI V. LEBEDEV and (in part) B. K. MERESHKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249—1388. Compare A., 1911, i, 26, 774, 959; 1912, i, 173).—The vast majority of organic compounds are essentially unstable, and their great variety owes its existence to what the author terms passive resistance. It is quite conceivable that polymerisation, as a process directing molecules into more stable forms, is very widespread, and that most unsaturated organic compounds are able to polymerise under suitable conditions. No sharp line can be drawn between association and polymerisation, although with typical association no difference can be found between the chemical reactions of the monomeride and of the polymeride; it may be that, owing to ready dissociation of the latter, only the former reacts or that no sufficiently sensitive reagent for the polymeride has been discovered. The stability of the complex molecule depends on the particular type of polymerisation occurring, in addition to the properties of the individual compound.

In the great majority of cases polymerisation occurs with formation of a ring system, the ring having in all cases an even number of atoms. In studying polymeric changes, account must be taken of the isomerisa-

tion so common with unsaturated compounds, especially with rise of temperature.

Among the hydrocarbons the principal well-defined types of polymerisation are : (1) the styrene type, peculiar to ethylenic hydrocarbons with unsymmetrical substitution of the hydrogen atoms by definite groups (phenyl), and yielding polymerides of high molecular weight and structures not yet definitely established; (2) the stilbene type, exhibited by ethylene derivatives with symmetrical replacement of the hydrogen atoms by certain groups (phenyl); (3) the acetylene type, giving benzene derivatives; (4) the allene type, yielding *cyclo*butane derivatives; (5) the divinyl [$\Delta^{\alpha\gamma}$-butadiene] type, which forms *cyclo*hexane derivatives and polymerides of uncertain constitution. If it can be shown that stilbene forms a polymeride and styrene a dimeride of closed-chain structure, types (1) and (2) may have to be regarded as a single type; and, further, the resemblance between polymerides of the styrene and divinyl types (compare Ostromisslenski, A., 1912, i, 280) may lead to the fusion of these two types. Most cases of polymerisation of unsaturated compounds containing halogen, nitrogen, oxygen, or sulphur may be referred to one of the above types.

Polymerisation of the divinyl or $\Delta^{\alpha\gamma}$-butadiene type is first considered, an account being given of all such hydrocarbons studied in this respect. Experiments with isoprene and with di*iso*propenyl [$\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene] show that : (1) the relative proportions of dimeride and polymeride formed increase and diminish respectively as the temperature is raised; (2) at constant temperature, the ratio between the proportions of dimeride and polymeride does not change during the heating ; (3) the reaction of polymerisation is sensitive to catalytic action, since replacement of the air in the tube by nitrogen results (with $\beta\gamma$ dimethyl-$\Delta^{\alpha\gamma}$-butadiene) in a fall of the relative amount of polymeride from 23% to 16·4%. It is further found that symmetrical hydrocarbons of this type, such as $\Delta^{\alpha\gamma}$-butadiene and its $\beta\gamma$-dimethyl derivative, yield a single dimeride, whereas the unsymmetrical isoprene gives two dimerides. In contradiction to the statement of Kondakov ("Synthetic Caoutchouc, its Homologues and Analogues," Yuriev, 1912, p. 101) and of Harries (A., 1911, i, 798), it is found that polymerisation of the pure hydrocarbons, without catalyst, yields no open-chain dimeride.

In general, it seems that no such equilibrium as that represented by dimeride ⇌ monomeride ⇌ polymeride exists, but that the processes of polymerisation are irreversible and proceed simultaneously in two directions, yielding dimeride and polymeride respectively. The existence of reversible processes of formation of dimeric and of polymeric forms renders it probable that such equilibria may yet be realised.

The possible methods of formation and structures of dimerides and polymerides are discussed in detail.

The dimeride of di*iso*propenyl [$\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene] is 4 : 6-dimethyldipentene or 4 : 6-dimethyl-$\Delta^{6,8(9)}$-menthadiene,

$$CMe\!<\!\substack{CMe\cdot CH_2\\CH_2\cdot CH_2}\!>\!CMe\cdot CMe\!:\!CH_2,$$
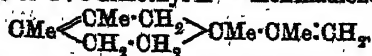
which is a colourless liquid with an aromatic odour, b. p. 85°/13 mm.,

$205°/750$ mm., $D_4^0\ 0.8741$, $D_0^{20}\ 0.8597$, $n_C^{197}\ 1.47716$, $n_D\ 1.48074$, $n_F\ 1.48796$, $n_G\ 1.49491$ (compare Richard, A., 1911, i, 733). Treatment with ozone in chloroform solution at $-20°$ yields the *ozonide*, $C_{12}H_{20}O_6$, which is a froth-like, amorphous compound, exploding violently on heating, but failing to yield the triketone on decomposition with water. Oxidation of the dimeride in aqueous acetone by means of permanganate yields: (1) δ-*Methyl-δ-isopropenyl-$\beta\eta$-octandione*,

$$CH_3\cdot CO\cdot CH_2\cdot CMe(\cdot CMe\dot{:}CH_2)\cdot CH_2\cdot CH_2\cdot CO\cdot CH_8,$$
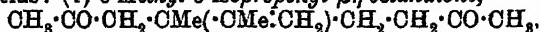
which is a viscous liquid, b. p. $132—133°/8.5$ mm., and yields the *semicarbazone*, $C_{14}H_{26}O_2N_6$, m. p. $228°$; hydrogenation of the diketone at the ordinary temperature in presence of platinum black gives δ-*methyl-δ-isopropyl-$\beta\eta$-octandione*, $CH_3\cdot CO\cdot CH_2\cdot CMePr^\beta\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$, as a colourless, viscous liquid, b. p. $133—135°/8$ mm., $D_4^{20}\ 0.9934$, the corresponding *semicarbazone*, m. p. $202°$, being also prepared. (2) A small proportion of an acid, m. p. $164—166°$, containing 63.2% of carbon and 8.88% of hydrogen.

Oxidation of the dimeride of $\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene by means of benzoylhydroperoxide in ethereal solution (compare Prileschaev, A., 1911, i, 255) yields (1) a small proportion of the *monoxide*,

$$OMe\!<^{OMe\cdot CH_2}_{CH_2\cdot CH_2}\!>\!OMe\cdot OMe\!<^{CH_2}_{O},$$
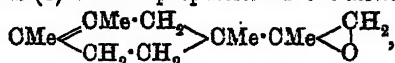
b. p. $94—95°/10$ mm., and (2) the *dioxide*, $C_{12}H_{20}O_2$, b. p. $110—112°/10$ mm., which when heated in a sealed tube at $115°$ with water acidified with benzoic acid gives the tetrahydric alcohol (4:6-*limonetritol*), $OH\cdot \dot{O}Me\!<^{OMe(OH)\cdot CH_2}_{CH_2———CH_2}\!>\!OMe\cdot OMe(OH)\cdot CH_2\cdot OH$, as a highly viscous liquid; oxidation of this by means of aqueous permanganate gave a small yield of the *keto-glycol*,

$$OH\cdot OMe\!<^{OMe(OH)\cdot CH_2}_{CH_2———CH_2}\!>\!OMe\cdot COMe,$$
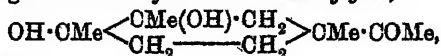
m. p. $155—165°$.

The action of dry hydrogen chloride on the dimeride in carbon disulphide yields $1:2:4$-*trimethyl-4-chloroisopropyl-Δ^1-cyclohexene*, $OMe\!<^{OMe\cdot CH_2}_{CH_2\cdot CH_2}\!>\!OMe\cdot OMe_2Cl$, which is a colourless liquid, b. p. $122—124°/17$ mm.

The polymeride of diisopropenyl is shown by means of its ozonide to have the structure $(\cdot CH_2\cdot OMe\dot{:}OMe\cdot CH_2\cdot CH_2\cdot OMe\dot{:}OMe\cdot CH_2\cdot)_x$. The *ozonide*, $C_6H_{10}O_8$, separates partly in a gelatinous form and yields acetonylacetone when heated with water (compare Harries, A., 1911, i, 798).

Further details are given of the results obtained with isoprene (compare A., 1911, i, 26). For obtaining pure isoprene use was made of the following method elaborated in Favorski's laboratory and not yet published. Crude isoprene, b. p. $30—40°$, obtained by decomposition of turpentine, is poured into a cooled solution of hydrogen bromide in acetic acid, and the precipitated mixture of bromides washed and dried. Amyl bromide is distilled off at $52—53°$ under 100 mm. pressure, and the residual $\alpha\gamma$-dibromo-γ-methylbutane, after distillation at $80—82°$ under 23 mm. pressure, heated at $150°$ with a large excess

of pounded potassium hydroxide in a flask provided with a dephlegmator and condenser ; the dibromide and monobromide formed from it are arrested by the dephlegmator and fall back into the flask, whilst the isoprene passes over and is condensed.   The isoprene thus obtained, distilled over sodium, has b. p. 34·5—35°, D_0^{20} 0·6803, n_D^{20} 1·42207, n_C 1·41787, n_F 1·43307, n_G 1·44280, optical exaltation (D) 1·07 (compare Harries and Neresheimer, A., 1911, i, 798).

Two dimerides of isoprene were obtained : (1) Dipentene, b. p. 58°/9·5 mm., 174—175°/760 mm., D_0^0 0·8607, D_0^{20} 0·8454, $n_D^{19\cdot7}$ 1·47428, n_C 1·47069, n_F 1·48211, n_G 1·48887.   (2) 1 : 3-Dimethyl-3-ethenyl-Δ^6-*cyclo*hexene (*loc. cit.*), D_0^0 0·8481, $n_D^{19\cdot7}$ 1·46581, n_C 1·46230, n_F 1·47204, n_G 1·47964, which yields a liquid tetrabromide, not obtained pure, and combines with 2HBr in acetic acid solution, giving the *compound*, $C_{10}H_{18}Br_2$, softening at 25° and melting at 34—35°.   1 : 3-Dimethyl-3-ethyl*cyclo*hexane (*loc. cit.*), obtained by hydrogenation of this dimeride in presence of platinum black and under a pressure of 70 atmospheres, has D_4^0 0·8132, D_4^{20} 0·7990, n_D^{20} 1·44112.   The *ozonide*, $C_{10}H_{16}O_6$, of this dimeride resembles those of di*iso*propenyl and dipentene and, on decomposition, gives an oil resolved on boiling into the *ketodialdehyde*, $COMe \cdot CH_2 \cdot CMe(CHO) \cdot CH_2 \cdot CH_2 \cdot CHO$, which yields α-methyl-α-acetonylglutaric acid on oxidation.   Treatment of the dimeride with benzoylhydroperoxide yields (1) the monoxide, which is a liquid, b. p. 68—70°/15 mm., with a camphor-like odour, and (2) the *dioxide*,

$$O<^{CMe——CH_2}_{CH \cdot CH_2 \cdot CH_2}>CMe \cdot CH<^O_{CH_2}$$, which is a liquid with an aromatic

odour, b. p. 108—109°/15 mm., and yields the *compound*, $C_{10}H_{20}O_4$, on hydration.

Two isomeric polymerides of isoprene are possible theoretically, and should give ozonides of the structures :

$$(1) \qquad [\cdot CH_2 \cdot CMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot CMe \cdot CH \cdot CH_2 \cdot]_x$$
$$\diagdown O_3 \qquad\qquad \diagdown O_3$$

$$and \cdot (II) \qquad [\cdot CH_2 \cdot CMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot CH \cdot CMe \cdot CH_2 \cdot]_x$$
$$\diagdown O_3 \qquad\qquad \diagdown O_3$$
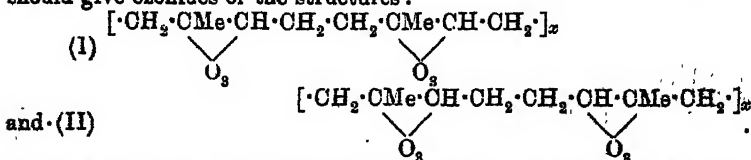
Of these, (I) corresponds with natural caoutchouc and should give, on decomposition, lævulinaldehyde and its peroxide, and lævulic acid ; all these products were actually observed.   Similarly, (II) should give succindialdehyde, succinic acid and acetonylacetone, none of which could be detected.   Hence, only the former polymeride is formed ; its *ozonide*, $C_5H_8O_3$, is an extremely viscous liquid, exploding when heated.

Piperylene should yield, not a dimeride of the structure,

$$CMe<^{CH—CH_2}_{CH_2 \cdot CH_2}>CH \cdot CH:CHMe$$
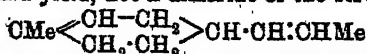
(compare Harries, this vol., i, 284), but two dimerides, formed thus :

$$(1) \; CH_2 \cdot CH \cdot CH \cdot CH \cdot CH_2 \cdot \; \rightarrow \; CH<^{CH—CH_2}_{CHMe \cdot CH_2}>CH \cdot CH:CHMe,$$

$$and \; (2) \; {^{CH_2}_{CH \cdot CH \cdot CH \cdot CH_2}} \; \rightarrow \; CH<^{CH—CHMe}_{CH_2 \cdot CHMe}>CH \cdot CH:CH_2;$$
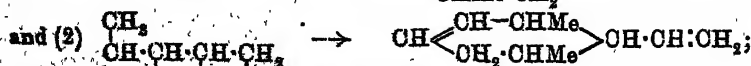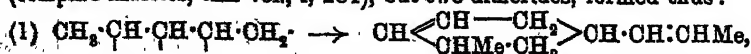
the former should have the higher boiling point.

According to a private communication from Favorski, di*iso*crotyl [$\beta\epsilon$-dimethyl-$\Delta^{\alpha\delta}$-hexadiene] undergoes spontaneous change into a waxy substance, but this was not observed by the author. This hydrocarbon undergoes polymerisation with great difficulty, only 50% of it being transformed after being maintained at 290° for ten days. The employment of such a high temperature causes partial isomerisation of the dimeride, of which only a single one should be formed from a symmetrical molecule, and also results in decomposition of the polymeride. The dimeride is 3:3:5:5:6:6-*hexamethyl*-4-*iso*crotyl-Δ^1-cyclo*hexene*, $CH{<}{CH-CMe_2 \atop CMe_2 \cdot CMe_2}{>}CH \cdot CH{:}CMe_2$, b. p. 130—132°/ 24 mm., D_4^0 0·8634, D_4^{20} 0·8491, n_D^{20} 1·47751, n_C 1·47452, n_F 1·48757, n_G 1·49120. The polymeride was obtained only as an impure, yellow, viscous liquid containing decomposition products.

Myrcene, which probably consists of a mixture of two or more isomerides, was found to have the constants: b. p. 56—57°/12 mm., D_4^{20} 0·7982, n_D^{20} 1·47065, n_C 1·46675, n_F 1·48055, n_G 1·48905. When heated for twelve days at 150°, it yields (1) two cyclic isomerides of myrcene, (a) b. p. 60—61·5°/16 mm., D_4^{20} 0·8392, n_D^{20} 1·46611, n_C 1·46270, n_F 1·47334, n_G 1·47974, and (b) b. p. 65—65·5°/16 mm., D_4^{20} 0·8340, n_D^{20} 1·47133, n_C 1·46774, n_F 1·47922, n_G 1·48613; (2) a dimeride, b. p. 183—184°/10 mm., D_4^{20} 0·8763, $n_D^{20\cdot1}$ 1·49859, n_C 1·49568, n_F 1·50668, n_G 1·51606; (3) a viscous polymeride yielding a mixture of products when treated with ozone (compare Harries, A., 1902, i, 811).

a-Phenyl-$\Delta^{\alpha\gamma}$-butadiene polymerises with great ease. The dimeride was investigated by Riiber (A., 1904, i, 569), who suggested formulæ for it and for the tribasic acid yielded on oxidising it with permanganate. The author regards these formulæ as inaccurate, since, according to his scheme, the dimeride should have the structure

$$CH{<}{CH-CH_2 \atop CHPh \cdot CH_2}{>}CH \cdot CH{:}CHPh,$$
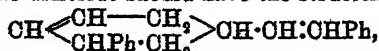
and the tribasic acid, $CO_2H \cdot CHPh \cdot CH_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H$, the latter agreeing better with the analytical data than that proposed by Riiber.
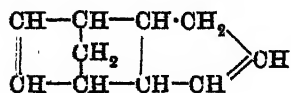
As was shown by Stobbe and Reuss (A., 1912, i, 842), *cyclo*pentadiene polymerises so rapidly that intense cooling is necessary in order to obtain it in the monomeric form. If the type of polymerisation exhibited by openchain hydrocarbons holds also for cyclic compounds, the dimeride should have the annexed structure (compare Kraemer and Spilker, A., 1896, i, 289). This case is under investigation.

Allene hydrocarbons polymerise with great ease and, unlike those of the divinyl type, with velocities varying only within narrow limits. The character of the polymerisation is also different, the polymerides being *cyclo*butane derivatives and forming an uninterrupted series from di- to hexa-merides. Actually, however, the polymerisation of allene hydrocarbons is complicated by transformation to the type shown by those of the divinyl series. This occurs in two ways: (1) the allene hydrocarbons undergo isomeric change into divinyl derivatives with

comparative ease, and (2) the dimerides are cyclic derivatives of divinyl ; thus, that of allene has the structure

$$CH_2:C{<}{\stackrel{CH_2}{\underset{C(:CH_2)}{\frown}}}{>}CH_2,$$
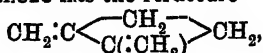
and readily polymerises giving a di-dimeride and a polymeride. At the ordinary temperature allene hydrocarbons polymerise so slowly that years elapse before the formation of an appreciable proportion of polymeride. But the temperature-coefficient of the velocity of the change is far greater than with divinyl derivatives, and at 150° the velocity is approximately the same as with isoprene and di*iso*propenyl. The author elaborates a scheme to explain the mechanism of the process, starting from the assumptions that the molecules combine initially at a single point and that the union is directed by two causes : the magnitude of the affinity with the unsaturated atoms and the polarity. The construction of models of the polymeric forms shows that two types of arrangement in space are possible : (1) the cyclic type, in which the central carbon atoms of allene are arranged in a ring in one plane, with the four-membered rings alternately on either side of this basal plane ; and (2) the spiral type, in which the central atoms of the allene groups are arranged in a spiral so that the first, fourth, and seventh carbon atoms occupy analogous positions on the spiral, and so on ; the four-membered rings lie in three mutually-perpendicular planes, the first, fourth, and seventh rings also taking up similar positions on the spiral. The dimerides of the two types are identical, as also are the trimerides. Stereoisomerism is possible, beginning with the tetrameride, and assuming the formation of polymeric forms according to both types, two stereoisomerides may be expected for the tetra-, penta-, and hexa-meride. Higher degrees of polymerisation are possible only with the spiral type.

When heated to 130—140°, *as*-dimethylallene gives 3% of dimeride, b. p. 140—141°, 18% of dimeride, b. p. 149—150°, 40% of dimeride, b. p. 179—181°, 33% of trimeride, b. p. 100°/8 mm., and 60% of vaseline-like residue. The three dimerides, which are the only possible ones, have been already described (A., 1912, i, 173). The *trimeride*,

$$CMe_2{<}{\stackrel{CH_2}{\underset{C(:CH_2)}{\frown}}}{>}C{<}{\stackrel{C(:CMe_2)}{\underset{CMe_2}{\frown}}}{>}CH_2,$$
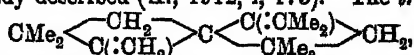
is a colourless, odourless liquid, b. p. 100°/8 mm., D_4^0 0·8723, D_4^{20} 0·8578, n_D^{20} 1·48724, n_C 1·48395, n_F 1·50260, n_G 1·51398, optical exaltation 2·28, and has the normal molecular weight in freezing benzene. Hydrogenation of the trimeride in presence of platinum black yields the *compound*, $CMe_2{<}{\stackrel{CH_2}{\underset{CHMe}{\frown}}}{>}C{<}{\stackrel{CHPr^a}{\underset{CMe_2}{\frown}}}{>}CH_2$, b. p. 116—118°/ 23 mm., D_4^0 0·8521, D_4^{20} 0·8380, $n_D^{19\cdot9}$ 1·46362, n_C 1·46101, n_F 1·47274, n_G 1·47827, optical exaltation 1·50. The ozonide of the trimeride is unstable, and was not obtained pure. Oxidation by means of benzoylhydroperoxide yields the *dioxide* (annexed formula), m. p. 49°, b. p. 137°/16 mm., which undergoes partial hydration to the *compound*, $C_{15}H_{26}O_3$, m. p. 136·5°,
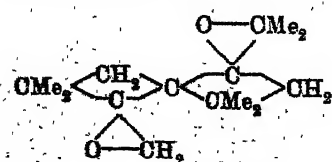
$$CMe_2{<}{\stackrel{CH_2}{\underset{C}{\frown}}}{>}C{<}{\stackrel{\stackrel{O—CMe_2}{\diagdown}}{\underset{OMe_2}{C}}}{>}CH_2$$

probably a glyco-oxide. Attempts to complete the hydration by heating with water containing a trace of acid resulted in the formation of a *diketone*, $C_{15}H_{24}O_2$, m. p. 86°, which yields a *semicarbazone*,

$$C_{17}H_{30}O_3N_6,$$

m. p. 170° (decomp.), but was not obtained in sufficient quantity to admit of the determination of its structure.

[With B. K. MERESHKOVSKI.]—When heated in a sealed tube at 150°, trimethylallene undergoes polymerisation and isomerisation, the mixture of dimerides consisting principally of 1 : 2-*dimethyl*-3 : 4-*di-isopropylidene*cyclo*butane*, $\begin{array}{c} \text{CHMe·C:CMe}_2 \\ | \\ \text{CHMe·C:CMe}_2 \end{array}$, which is a colourless liquid with the odour of kerosene, b. p. 69—70°/11 mm., 190—191°/754 mm., D_4^{20} 0·8247, n_D^{20} 1·48337, n_C 1·47946, n_F 1·49282, n_G 1·50297. The ozonide is unstable, and on distilling in a current of steam is decomposed into dimethylsuccinic acid, acetone peroxide, and 1 : 2-*dimethyl*-3 isopropylidene cyclo*butan*-4-*one*, $\begin{array}{c} \text{CHMe·C:CMe}_2 \\ | \\ \text{CHMe·CO} \end{array}$, which is a colourless liquid with the characteristic quinone-like odour common to all unsaturated ketones obtained from dimerides of allene hydrocarbons, b. p. 83—86°/20 mm., and was not obtained free from traces of the original dimeride; its *semicarbazone*, $C_{10}H_{17}ON_3$, m. p. 200—201° (decomp.), contained a small proportion of another semicarbazone, m. p. about 180°; oxidation of the ketone with permanganate yields the maleinoid form of dimethylsuccinic acid. Products of higher polymerisation are formed to the extent of 10%, but no individual compounds were isolated.

[With B. K. MERESHKOVSKI.]—At 150°, polymerisation of s-dimethylallene is complete in four to five days. The products contain (1) about 90% of the dimeride, 1 : 2-*dimethyl*-3 : 4-*diethylidene*cyclo*butane*, $\begin{array}{c} \text{CHMe:C·CHMe} \\ | \\ \text{CHMe:C·CHMe} \end{array}$, which is a colourless liquid, b. p. 65°/22 mm.; 163°/762 mm., D_4^{20} 0·8113, n_D^{20} 1·47850, n_C 1·47423, n_F 1·48913, n_G 1·49838, optical exaltation 2·25. When oxidised with permanganate, this dimeride yields the maleinoid form of s-dimethylsuccinic acid and acetic acid (?), whilst hydrogenation at ordinary temperature in presence of platinum black yields 1 : 2-*dimethyl*-3 : 4-*diethyl*cyclo*butane*, $\begin{array}{c} \text{CHEt·CHMe} \\ | \\ \text{CHEt·CHMe} \end{array}$, b. p. 155—156°/760 mm., D_4^{20} 0·7729, n_D^{20} 1·42447, n_C 1·42193, n_F 1·42950, n_G 1·43377, optical exaltation 0·24; (2) about 5% of the *trimeride*, $\text{CHMe} \big\langle {}^{\text{CHMe}}_{\text{C(:CHMe)}} \big\rangle \text{C} \big\langle {}^{\text{C(:CHMe)}}_{\text{CHMe}} \big\rangle \text{CHMe}$ (?), which is a colourless, odourless liquid, b. p. 108—110°/17 mm.

When heated at 140° for three and a-half days, allene yields 5% of dimeride, 15% of trimeride, 5% and 22% of tetramerides I and II, 18% of pentameride, 10% of hexameride, and 25% of residual polymeride. With the exception of the dimeride and tetrameride I, these polymeric forms all rapidly absorb atmospheric oxygen, and all without exception yield formic, oxalic, and succinic acids on oxidation, and give a dark brown coloration with tetranitromethane. The viscosity increases with the degree of polymerisation, the hexameride being somewhat more

liquid than glycerol. (1) The dimeride, 1 : 2-*dimethylenecyclobutane*, $\begin{smallmatrix}CH_2 \cdot C:CH_2\\ CH_2 \cdot C:CH_2\end{smallmatrix}$ is a colourless liquid, b. p. 63—65°, D_4^{20} 0·7698,

n_D^{20} 1·42317. (2) The *trimeride*, $CH_2{<}{\begin{smallmatrix}CH_2-\\ C(:CH_2)\end{smallmatrix}}{>}C{<}{\begin{smallmatrix}C(:CH_2)\\ -CH_2\end{smallmatrix}}{>}CH_2$, is a liquid with a peculiar odour, b. p. 135°/774 mm., 70·5°/90 mm., 38°/21 mm., D_4^{20} 0·8624, n_D^{20} 1·48064, n_C 1·47677, n_F 1·48922, n_G 1·49694, optical exaltation 1·04. It readily absorbs hydrogen in presence of platinum-black giving the *compound*,

$$CH_2{<}{\begin{smallmatrix}CH_2\\ CHMe\end{smallmatrix}}{>}C{<}{\begin{smallmatrix}CHMe\\ CH_2\end{smallmatrix}}{>}CH_2,$$
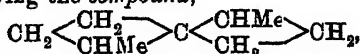
which is a colourless, almost odourless liquid, b. p. 132°/756 mm., D_4^{20} 0·7972, n_D^{20} 1·43459, n_C 1·43159, n_F 1·43950, n_G 1·44410, optical exaltation 1·23. (3) Tetrameride I is a *dimeride of the dimeride*, $\begin{smallmatrix}CH_2 \cdot C \cdot CH_2 \cdot CH_2\\ CH_2 \cdot C——CH_2\end{smallmatrix}{>}C{<}{\begin{smallmatrix}CH_2-\\ C(:CH_2)\end{smallmatrix}}{>}CH_2$, and forms a colourless liquid with an odour of turpentine, b. p. 72—74°/9 mm., D_4^{20} 0·8955, n_D^{20} 1·50301, n_C 1·49905, n_F 1·51204, n_G 1·51999, optical exaltation 2·58. On prolonged heating in a sealed tube at 150°, it thickens and deposits an insoluble polymeride, which was obtained only in small amount. With hydrogen in presence of platinum-black, it gives the *compound*, $\begin{smallmatrix}CH_2 \cdot CH \cdot CH_2 \cdot CH_2\\ CH_2 \cdot CH——CH_2\end{smallmatrix}{>}C{<}{\begin{smallmatrix}CH_2\\ CHMe\end{smallmatrix}}{>}CH_2$, as a colourless liquid with a faint odour, b. p. 77—78°/13·5 mm., D_4^{20} 0·8679, n_D^{20} 1·46809, n_C 1·46448, n_F 1·47305, exaltation 1·51. (4) *Tetra-*

(I.) $\begin{smallmatrix}CH_2 \cdot CH_2 \;\; CH_2 \cdot CH_2\\ C——C——C——C\\ CH_2 \;\; CH_2 \cdot CH_2 \;\; CH_2\end{smallmatrix}$

(II.) $\begin{smallmatrix}CH_2——CH_2 \;\; CH_2 \cdot CH_2\\ CHMe \cdot C——C——CHMe\\ CH_2 \cdot CH_2\end{smallmatrix}$
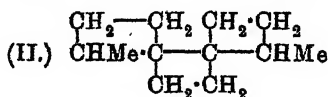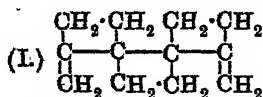
meride II (I.) is a colourless liquid with an odour of kerosene, b. p. 101°/10 mm., D_4^{20} 0·9346, n_D^{20} 1·52624, n_C 1·52210, n_F 1·53579, n_G 1·54396, exaltation 2·33, and has the normal molecular weight in freezing benzene. On hydrogenation it yields the *compound* (II.), b. p. 95°/13·5 mm., D_4^{20} 0·8827, n_D 1·48289, n_C 1·47950, n_F 1·48941, n_G 1·49528, exaltation 2·02. On oxidation it yields formic, oxalic, and succinic-acids. (5) The *pentameride* (annexed formula) is a viscous, almost odourless liquid, b. p. 131—132°/10·5 mm., D_4^{20} 0·9498, n_D^{20} 1·52814, n_C 1·52422, n_F 1·53765, n_G 1·54591, exalta-tion 2·90. On hydrogenation it takes up sufficient hydrogen to saturate two double linkings, giving the *compound*, $C_{15}H_{24}$, as a colourless liquid with a faint odour, b. p. 123·5—124·5°/8 mm., D_4^{2} 0·9152, n_D^{20} 1·49623, n_C 1·49265, n_F 1·50241, n_G 1·50810, exaltation 2·40, and exhibits normal cryoscopic behaviour in benzene. (6) The *hexameride*, $C_{18}H_{24}$, of similar structure to the foregoing, is a viscous, almost odourless liquid, b. p. 170°/10 mm., D_4^{20} 0·9721, n_D^{20} 1·53869, n_C 1·53426, n_F 1·54817, n_G 1·55648, exaltation 3·64. Oxalic and succinic acids were found among its products of oxidation.

$\begin{smallmatrix}CH_2 \cdot CH_2 \;\; CH_2 \cdot CH_2 \;\; CH_2\\ C——C——C——C——C\\ CH_2 \;\; CH_2 \cdot CH_2 \;\; CH_2 \cdot CH_2\end{smallmatrix}$

It has been shown by Favorski (A., 1891, 1330) that, when heated with alcoholic alkali hydroxide, hydrocarbons of the diallyl series undergo isomeric change to divinyl derivatives: $C:C\cdot C\cdot C:C:C \longrightarrow$ $C\cdot C:C:C\cdot C:C\cdot C$; thus diallyl yields $\Delta^{\beta\delta}$-hexadiene. When heated at 250° for ten days, diallyl begins to isomerise, 10% of the monomeride boiling at a higher temperature than diallyl. The crude polymeride consists of (1) about 15% of a liquid of peculiar odour, b. p. 97—98°/20 mm., consisting of mixed dimerides, and (2) about 85% of colourless, insoluble, caoutchouc-like polymeride, which is converted into ozonide only with difficulty. At 150°, $\Delta^{\beta\delta}$-hexadiene yields a dimeride, b. p. 88—90°/20 mm., quite different from that of diallyl, but at 250° it gives a considerable proportion of the dimeride, b. p. 96—98°/20 mm.

The author has devised a method for determining the velocity at which polymerisation occurs. From 2 to 10 grams of the hydrocarbon were sealed in tubes and heated in a perfectly dark thermostat at $159\pm0\cdot1°$. After definite intervals of time, the tubes were cooled and their contents introduced into tared distilling flasks connected with small condensers and tared receivers. Liquids with low boiling points were distilled at ordinary pressure and those with high boiling points under diminished pressure. A bath of Wood's metal was used. for the heating, its temperature being at first below the boiling point of the monomeride, and finally about the boiling point of the dimeride. The monomeride, the residual polymeride, and sometimes also the dimeride were weighed to within $0\cdot02$ gram. In general, all the polymerised products were taken into account in calculating the velocity. The results obtained in this way were corrected for several errors inherent in the method. The numbers obtained with twelve hydrocarbons of the $\Delta^{\alpha\gamma}$-butadiene series show that: (1) With isomerides, the transference of a substituent from the extreme atom of a conjugated system of atoms to the middle atom is accompanied by increase in the velocity of polymerisation, and conversely. (2) The formation of a ring from a chain containing a conjugated system increases the velocity of polymerisation. (3) In homologous series, increase of the mass of a substituent at the middle (or extreme) atoms of a conjugated system increases (or lowers) the velocity of polymerisation, assuming that the heating occurs at corresponding temperatures. The results given by the four allene derivatives lead to the following conclusions: (1) The velocity of polymerisation of isomeric hydrocarbons of the allene series does not depend on the positions of the substituent groups. (2) In an homologous series of allene hydrocarbons, increase of the mass of the substituent results in increased velocity of polymerisation, the heating being at corresponding temperatures. T. H. P.

Polymerisation as a Method of Detecting the Allene Group, $C:C:C$. Sergei V. Lebedev (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1390—1391).—The polymerisation of allene hydrocarbons affords a simple and easy method of distinguishing them from diethylenic hydrocarbons of other types. At 150° allene hydrocarbons are polymerised almost completely in one to two days, part undergoing isomeric change to $\Delta^{\alpha\gamma}$-butadiene derivative. The crude polymeride consists principally

of dimeride or, with unsymmetrical allene hydrocarbons, of dimerides. The dimeride is separated by distillation; when several are present, the predominating one is obtained by fractionation.   The dimeride is

of the type $\begin{smallmatrix} C \cdot C \vdots C \\ C \cdot C \vdots C \end{smallmatrix}$, and, on oxidation by means of permanganate in

acetone solution, gives a good yield of succinic acid or one of its substituted derivatives, these being well crystallised and readily transformed into anhydrides. Further, the dimerides of allene hydrocarbons exhibit marked optical exaltation, which is usually about, and greater than, 2; dimerides from diethylene hydrocarbons of other types are optically normal.   T. H. P.

Isomeric Transformations of Diethylenic Hydrocarbons. I. Isomeric Transformation of Dimethylallene. [γ-Methyl-Δ-ᵃ·ᵝ-butadiene] into Isoprene. L. M. KUTSCHEROV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1634—1654).—When heated with quinoline hydrobromide (compare Favorski and Borgmann, A., 1908, i, 15), γ-methyl-Δ-ᵃ·ᵝ-butadiene readily undergoes isomeric change into isoprene (50—55% yield) and a small proportion of *iso*propylacetylene [γ-methyl-Δ-ᵃ-butinene].   The reaction is irreversible, neither isoprene nor γ-methyl-Δ-ᵃ-butinene undergoing isomerisation under the above conditions; isoprene yields condensation products and combines with the pyridine, whilst γ-methyl-Δ-ᵃ-butinene partly remains unchanged and partly undergoes conversion into an unsaturated derivative according to the equation: $C_5H_8 + C_9H_7N,HX = C_5H_9X + C_9H_7N$.   The formation from γ-methyl-Δ-ᵃ·ᵝ-butadiene of isoprene is represented by the scheme: $CMe_2\!:\!C\!:\!CH_2 + C_9H_7N,HX \rightarrow CMe_2X\cdot CH\!:\!CH_2 + C_9H_7N \rightarrow CH_2\!:\!CMe\cdot CH\!:\!CH_2 + C_9H_7N,HX$, and that of γ-methyl-Δ-ᵃ-butinene by: $CMe_2\!:\!C\!:\!CH_2 + C_9H_7N,HX \rightarrow CHMe_2\cdot CX\!:\!CH_2 + C_9H_7N \rightarrow CHMe_2\cdot C\!:\!CH$; in the former case, the compound $CMe_2X\cdot CH_2\cdot CH_2X$ may also be formed as an intermediate product.

β-Bromo-γ-methyl-Δ-ᵃ-butene, $CH_2\!:\!CBr\cdot CHMe_2$, formed by treating γ-methyl-Δ-ᵃ-butinene either with hot quinoline hydrobromide or with hydrogen bromide in the cold, is a liquid, b. p. 100·5°/758 mm., D^{20} 1·2381 (1·2320), n_D^{20} 1·45093 (1·45033), and is reconverted into γ-methyl-Δ-ᵃ-butinene when heated in a sealed tube with alcoholic potassium hydroxide at 138°.   When treated with aqueous hydrobromic acid it yields: (1) γδ-dibromo-β-methylbutane, b. p. 61—62°/12 mm.; (2) *γγ-dibromo-β-methylbutane*, $CMeBr_2\cdot CHMe_2$, m. p. 13—15°, b. p. 53·5—54°/12 mm., 44—45°/8 mm., D_4^2 1·6987, D_4^{20} 1·6695, n_D^{20} 1·50468, which is converted into methyl *iso*propyl ketone when heated in a sealed tube with water and lead hydroxide.

γγδ-Tribromo-β-methylbutane, $CH_2Br\cdot CBr_2\cdot CHMe_2$, obtained by the action of bromine on β-bromo-γ-methyl-Δ-ᵃ-butene, is a hygroscopic liquid, b. p. 100—101·5°/12·5 mm., D_4^{20} 2·07112, n_D^{20} 1·55448.
                                                                   T. H. P.

Pyrogenic Acetylene Condensations. RICHARD MEYER and AUGUST TANZEN (*Ber.*, 1913, 46, 3183—3199. Compare A., 1912, i, 525).—The previous experiments in which nine hydrocarbons present in coal tar were obtained synthetically by the condensation of acetylene

have been repeated in an enlarged apparatus which enabled 6000 grams of tar to be obtained, which has been completely investigated. Phenanthrene and acenaphthene and also, in small quantities, styrene and hexylene were identified. The last has previously only been found in boghead coal and in bituminous shale.

On heating acetylene diluted with coal gas with hydrogen cyanide, pyridine and its homologues were obtained. Mixtures of ammonia and benzene yield aniline when heated, the reaction being reversible. Further condensation of the aniline leads to carbazole and to benzonitrile, the latter being formed by the action of hydrogen cyanide on aniline.

In all, therefore, seventeen constituents of coal tar have been identified as formed by the pyrogenetic condensation of acetylene. The hexylene formed is n-hexylene, identical with that from mannitol.

The formation of pyridine requires a temperature of 800°, at which the mixture of acetylene, hydrogen, and hydrogen cyanide can be heated without catching fire. Apparently the hydrogen cyanide acts as a poison towards the catalytic changes which bring about the sudden decomposition of acetylene and cause a mixture of acetylene and hydrogen to catch fire much below 800°.

The apparatus used is figured and described in detail.   E. F. A.

Improvements in the Preparation of Dichlorinated Hydrocarbons in which the Chlorine is Combined with Different Carbon Atoms. WILLIAM H. PERKIN, CHARLES WEIZMANN, and HAROLD DAVIES (Fr. Pat. 452503, and 1st Addition).—If vaporised hydrocarbons or chlorohydrocarbons are treated with the required halogen with or without the addition of a catalyst or in the presence of light with subsequent fractionation under diminished pressure definite products are obtained, and the preparation of the following compounds as chief products of the reaction is described.

From *isoamyl* chloride : *δ-dichloro-β-methylbutane* (b. p. 142°), *γδ-dichloro-β-methylbutane* (b. p. 150°), and *ββ-dichloro-β-methylbutane* (b. p. 170—172°).

From α-chlorobutane : tetrachlorobutane : from n-heptane : chloroheptane, and from *isoamyl* bromide : *ββ-dichloro-β-methylbutane* (b. p. 72—75°/5 mm.).

Monochloroacetic acid can also be prepared from acetic acid in a similar manner.   F. M. G. M.

Compounds of Aluminium Bromide with Hydrogen Sulphide and Organic Bromides. Synthesis of Mercaptans. VLADIMIR A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1162—1173. Compare A., 1907, i, 580).—The following compounds have been prepared : $AlBr_3,H_2S$, obtained by passing hydrogen sulphide through aluminium bromide, either in a fused condition or in solution in carbon disulphide, forms colourless crystals, m. p. about 84°, and is decomposed immediately by the moisture of the air with liberation of hydrogen bromide and hydrogen sulphide.

$AlBr_3,EtBr,H_2S$, obtained by passing hydrogen sulphide through a solution of aluminium bromide in ethyl bromide, forms snow-white

crystals, m. p. (in sealed capillary) about 81°, is readily decomposed by water with formation of mercaptan (90% yield) : $AlBr_3,EtBr,H_2S +$ aq. $= AlBr_3,$aq. $+ EtHS + HBr,$ and in solution attacks aluminium or zinc with liberation of hydrogen. Electrolysis of a solution of the compound in ethyl bromide with platinum electrodes results in the development of hydrogen at the cathode and bromine at the anode.

$AlBr_3,CH_2Br\cdot CH_2Br,H_2S$ forms a pale yellow, crystalline powder decomposing at about 200°, and is also decomposed by the moisture of the air with formation of an oil with a garlic-like odour.

$AlBr_3,CHBr_3,H_2S$ is decomposed by water, apparently with formation of thioformic acid, which then undergoes condensation.

The structures of these compounds are considered in the light of Werner's co-ordination system.   T. H. P.

Dipropyl*iso*amylcarbinol and the Action of Nickel Carbonate on its Chlorohydrin. IVAN VANIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1155—1162).—Zaicev (A., 1912, i, 777) has shown that the action of silver carbonate on 1-chloro-1-allyl*cyclo*hexane yields an unsaturated hydrocarbon, C_9H_{14}. The author finds that a similar change is effected by the action of nickel carbonate on ε-chloro-β-methyl-ε-propyloctane.

Dipropyl*iso*amylcarbinol (β-methyl-ε-propyloctan-ε-ol), obtained by the action of magnesium *iso*amyl bromide on butyrone, has properties agreeing well with those given by Murat and Amouroux (A., 1912, i, 527).

ε-*Chloro-β-methyl-ε-propyloctane*, $CPr_2Cl\cdot CH_2\cdot CH_2\cdot CHMe_2$, is a colourless, mobile liquid, b. p. 115—117°/30 mm., D_0^0 0·8901, D_0^{20} 0·8748. When heated with excess of nickel carbonate in a reflux apparatus in an oil-bath at 135—145° for four to five hours, it is converted into a *methylpropyloctene*, $CHEt:CPr\cdot CH_2\cdot CH_2\cdot CHMe_2$ or $CPr_2:CH\cdot CH_2\cdot CHMe_2$, b. p. 89—91°/20 mm., 189—191°/756·5 mm., D_0^0 0·7773, D_0^{20} 0·7610, which may be identical or isomeric with that obtained by Murat and Amouroux (*loc. cit.*) by catalytic dehydration of dipropyl*iso*amylcarbinol with alumina.   T. H. P.

Transformation of *iso*Nitro-compounds into Ketones. S. S. NAMETKIN and (Mlle.) E. I. POZDNJAKOVA (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1420—1422).—Three methods exist for converting secondary nitro-compounds into ketones : (1) Reduction of nascent *iso*nitro-compounds by means of stannous chloride (compare Konovalov, A., 1899, i, 733) ; (2) action of acids on aqueous solutions of salts of *iso*nitro-compounds (compare Nef, A., 1895, i, 3) ; (3) heating of halogen-substituted nitro-compounds (compare Wislicenus and his collaborators, A., 1908, i, 973 ; 1909, i, 99 ; 1910, i, 621 ; 1912, i, 52). The last two methods are, however, only of theoretical interest. Nef's method yields, besides the ketone (or aldehyde), more or less free nitro-compound, which renders purification difficult, whilst method (3) is applicable only to those cases in which aggregation of several electro-negative groups to one carbon atom renders the halogen-

substituted nitro-compound unstable. Konovalov's method gives excellent results.

Investigation of the action of permanganate on nitro-compounds (compare A., 1910, i, 830; Konovalov, A., 1904, i, 499; 1905, i, 762) shows that, under the following conditions, almost quantitative yields of the corresponding ketones are obtained. A solution of the nitro-compound in potassium hydroxide solution (1 part to 2 of water) is mixed with five to six times its volume of water, and in the event of separation of insoluble nitro-compound, the latter is extracted by means of light petroleum. To the aqueous solution, mixed with pieces of ice in a large flask, is gradually added the theoretical quantity of $1\cdot5\%$ potassium permanganate solution, the ketone being subsequently distilled in a current of steam.

In this way, nitro*cyclo*hexane gave a 97% yield of *cyclo*hexanone, and nitrofluorene, a 96% yield of fluorenone.　　　　T. H. P.

Structure of *iso*Nitro-compounds. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1414—1420).—The author criticises the arguments advanced by Steinkopf and Jürgens (A., 1912, i, 152) in support of Hantzsch's formula for *iso*nitro-compounds.

Stress is laid on the unsaturated character of these compounds, which react with halogens and halogen hydracids, and in alkaline solution, even in the cold, instantly reduce 1—2% potassium permanganate solution, the nitro-compounds being converted almost quantitatively into ketones (compare preceding abstract). Such ready oxidisability is difficult to explain according to Hantzsch's ring constitution, but is easily understood if the presence of a double linking is assumed as is the case in the structure proposed by Michael and Nef. If oxidation at a double linking between carbon and nitrogen follows the same course as at one between two carbon atoms, the initial product of the reaction should be a compound exhibiting an accumulation of hydroxyl groups and hence possessing but slight stability; loss of the elements of water from this compound would yield ketone and a nitrite: $=C{:}NO{\cdot}OK \longrightarrow =C(OH){\cdot}NO(OH)(OK) \longrightarrow =CO + KNO_2 + H_2O$.

The behaviour of salts of primary nitro-paraffins on acidification, which yields transitory nitroso-compounds, and finally hydroxamic acids, is also readily accounted for on the basis of Michael and Nef's formula: $CHR{:}NO{\cdot}OH \longrightarrow CHR{:}O + {:}NOH \longrightarrow CHR(OH){\cdot}NO \longrightarrow CR(OH){:}NOH$. When, however, the nitro-group is accompanied by a more or less electronegative group, this intermediate formation of nitroso-compound does not take place, as no blue or green coloration then makes its appearance. Such an essential variation in one and the same reaction leads the author to suggest that the first stage in the action of dry hydrogen chloride is most probably a direct combination, the unstable compound thus formed subsequently undergoing intramolecular rearrangement and loss of water: $CHR{:}NO{\cdot}OH + HCl \longrightarrow CHRCl{\cdot}NH(OH){:}O \longrightarrow CHRCl{\cdot}N(OH)_2 \longrightarrow CRCl{:}NOH$. In those cases where the *iso*nitro-compound and the product of its union with the hydrogen haloid exhibit particularly slight stability,

the loss of water may partly precede the rearrangement ; a nitroso-compound would then be formed as intermediate product :

$$CHR\dot{:}NO\cdot OH \longrightarrow CHRCl\cdot NH(OH)\dot{:}O \longrightarrow CHRCl\cdot NO \longrightarrow CRCl\dot{:}NOH.$$

Analogous interpretations suggest themselves for the formation of halogen-substituted nitro-products, nitrolic acids and ψ-nitroles. Further, Nef's reaction does not necessitate the intermediate formation of a ring compound, as it is expressed in all probability by the scheme:

$$:C:NO\cdot OH + H_2O \longrightarrow :C(OH)\cdot NH(OH)\dot{:}O + H_2O \longrightarrow :C(OH)_2 +$$
$$:NOH + H_2O. \hspace{4cm} T. H. P.$$

Nitrosites of the Aliphatic Series. K. V. SIDORENKO (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1585—1604).—The author has devised an improved method for preparing ethylene nitrosite (compare Demjanov, A., 1899, i, 845), a number of reactions of this compound being studied.

When heated in a sealed tube with dilute hydrochloric acid (1 : 1), it yields hydroxylamine, apparently according to the equation :

$$(C_2H_4O_3N_2)_2 + 4H_2O + 4HCl = 2CHO\cdot CO_2H + 4NH_2\cdot OH,HCl.$$
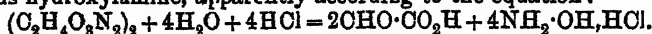
At the ordinary temperature it is dissolved by concentrated sulphuric acid, from which it is precipitated unchanged on dilution. Nitric acid seems to be without action on it in the cold, but in the hot yields oxalic acid.

With aniline in absolute alcoholic solution, it gives a basic compound, and this, with hydrochloric acid, yields a crystalline substance, which is difficult to purify and gives poor results on analysis. Under similar conditions, p-nitroaniline acts on it apparently as a catalyst, being obtainable unchanged from the products of the reaction.

With benzylamine it reacts in accordance with the equation :

$$(C_2H_4O_3N_2)_2 + NH_2\cdot CH_2Ph = (C_2H_4O_2N_2)_2\cdot N\cdot CH_2Ph + N_2O + H_2O,$$

the unstable *compound* thus obtained crystallising in long, colourless, silky prisms and exhibiting normal cryoscopic behaviour in benzene.

With dibenzylamine it reacts thus : $(C_2H_4O_3N_2)_2 + 2NH(CH_2Ph)_2 = 2C_2H_4O_2N\cdot N(CH_2Ph)_2 + N_2O + H_2O$, the compound formed crystallising in long prisms, m. p. $74\cdot6$—$75\cdot2°$, and possessing the normal molecular weight in freezing benzene. This compound exhibits feeble basic properties ; it exerts a scarcely perceptible alkaline reaction on litmus, and yields no salts, even with strong acids. When reduced with tin and hydrochloric acid, it yields a sparingly soluble hydrochloride, which forms a platinichloride insoluble in alcohol. Accompanying the dibenzylamine derivative is a small quantity of a compound which separates in crystalline granules and possibly represents the result of combination between the amine and the nitrosite after the latter is resolved into two separate molecules.

From these results the conclusion is drawn that ethylene nitrosite has the structure $N_2O_2(CH_2\cdot CH_2\cdot NO_2)_2$, and thus belongs to the class of ψ-nitrosites (compare Wieland, A., 1904, i, 54). T. H. P.

The History of Alcohol. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1913, **37**, 1313—1315, 1346—1347, 1358—1361, 1419—1422, 1428—1429. Compare A., 1912, i, 824 ; ii, 897).—A reply, with

historical quotations, to criticism by Diels of the author's view that alcohol and the process of distillation of readily volatile substances were unknown before the eleventh century. H. W.

Vapour Pressure of Glyceryl Trinitrate at the Ordinary Temperature. D. CHIARAVIGLIO and O. M. CORBINO (*Gazzetta*, 1913, 43, ii, 390—398).—In certain circumstances the rate of cooling of a warm substance situated in a closed space containing a very attenuated gas or vapour is proportional to the concentration of the molecules of the gas or vapour. Applying this method, the authors find that at about 21° the vapour pressure of glyceryl trinitrate is less than 0·0001 mm., so that it is beyond the limits of measurement or even detection. The value for the vapour pressure given by Marshall (*J. Soc. Chem. Ind.*, 1904, 23, 157; compare P., 1913, 29, 157) they regard as untrustworthy, because it is based on the assumption that, since the vapour pressures of glyceryl trinitrate and mercury are equal at 70°, they are also equal at the ordinary temperature. R. V. S.

Preparation of Aluminium Ethoxide. CLÉMENT BERGER (*Compt. rend.*, 1913, 157, 717—718).—Aluminium amalgam acts but slowly on absolute alcohol, but if, prior to the addition of the amalgam, a little sodium is dissolved in the alcohol, then, on warming the mixture under a reflux condenser, a rapid action takes place. When a considerable precipitate has formed, it is filtered off rapidly, and the filtrate evaporated to dryness in a vacuum. The solid residue is *aluminium ethoxide*, Al(OEt)$_3$. It is readily decomposed in the solid state or in solution by water, giving alcohol and aluminium, the presence of small quantities of water stopping its preparation. In the solid state it is decomposed by heat. W. G.

Preparation of Epichlorohydrin. JEAN NIVIERE (*Bull. Soc. chim.*, 1913, [iv], 13, 969—971).—A detailed account of a method already mentioned (compare this vol., i, 697) for the preparation of epichlorohydrin by the interaction of αγ-dichlorohydrin and potassium hydroxide in the presence of small quantities of water. W. G.

Catalytic Preparation and Decomposition of Esters. ALPHONSE MAILHE (*Chem. Zeit.*, 1913, 37, 777—778, 806—807).— The first paper contains a historical account of the work done on the catalytic preparation and decomposition of esters with particular reference to the more recent experiments of Sabatier and Mailhe on the use of metallic oxides. The second paper is a discussion of the behaviour of esters of aliphatic acids towards metallic oxide catalysts with special reference to formic acid and its esters. H. W.

Preparation of Sparingly Soluble Salts of Aluminium with Formic Acid Alone or with Formic together with Acetic Acid. ALBERT FRIEDLÄNDER (D.R.-P. 263865).—*Aluminium formate*, Al(OH)(HCO$_2$)$_2$, and *aluminium formoacetate*,
$$\text{HCO}_2 \cdot \text{Al(C}_2\text{H}_3\text{O}_2)\text{OH,2H}_2\text{O,}$$

are respectively prepared by heating aluminium hydroxide with anhydrous formic acid or with a mixture of formic and acetic acids ; they are of therapeutic value.   F. M. G. M.

Ferri- and Chromi-formates. RUDOLF F. WEINLAND and HANS REIHLEN (*Ber.*, 1913, **46**, 3144—3150).—The compounds formed when a ferric salt is treated with sodium formate have been studied.   In the deep red solution which results when equivalent quantities are mixed there is present the cation $[Fe_3(H \cdot CO_2)_6]$ of the hexaformato-triferri-base, of which only the monoformate has yet been isolated (Belloni, A., 1909, i, 283 ; Tower, 1910, ii, 900). By the addition of solid sodium formate to such a solution, the red colour gradually becomes pale, and *trisodium hexaformatoferrate*, $[Fe(H \cdot CO_2)_6]Na_3$, separates in pale green, microscopic, rectangular tablets. Thus, in presence of much sodium formate the anion $[Fe(H \cdot CO_2)_6]$ of hexaformatoferric acid is formed. This recalls the deep green of the trioxalatoferri-anion. By the action of water, the pale green solution or salt becomes red, the complex ions being in equilibrium.

The composition of the red formates, which are formed when ferric salts are mixed with sodium formate, varies, and the formic acid content rises with the concentration of that acid in the solution.   It is therefore probable that in these substances there may be present salts of the hexaformatoferri-base with the hexaformatoferric acid Brick-red, microcrystalline *compounds* which agree with the formulæ $[Fe(H \cdot CO_2)_6][Fe_3(H \cdot CO_2)_6],8H_2O$ and

$$\left[Fe(H \cdot CO_2)_6\right]\left[Fe_3 {(H \cdot CO_2)_6 \atop (OH)_2}\right]_3,14H_2O$$
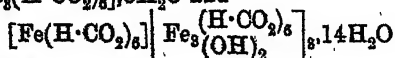
have been prepared.

Similar phenomena occur in the case of chromium salts. From a solution containing 30 mols. of sodium formate to one of chromium nitrate, *trisodium hexaformatochromate*, $[Cr(H \cdot CO_2)_6]Na_3.4 \cdot 5H_2O$, crystallises in greenish-violet rhombohedra, which are only decomposed by ammonia after prolonged boiling.   J. C. W.

Two Isomeric Forms of Anhydrous Sodium Acetate. DANIEL VORLÄNDER and OTTO NOLTE (*Ber.*, 1913, **46**, 3199—3212).—An anhydrous form of sodium acetate is obtained on fusing sodium acetate trihydrate below 100°, and it also crystallises from fused sodium acetate. Intermediate hydrates do not exist. This modification is isomeric with that obtained on cooling the amorphous flux prepared by dehydrating above 200°. The new low temperature modification crystallises in the rhombic system and passes into the isomeride at 198°. The change is enantiotropic, the reverse change taking place so slowly that the two forms can exist side by side for months. The decomposition temperature of the trihydrate into water and anhydride is 58·2°.

Both anhydrous forms when crystallised from absolute ethyl or methyl alcohol yield the new rhombic form. This is an excellent condensation-agent, absorbing water much more quickly than the ordinary fused form. For such purposes the trihydrate is best dehydrated at 120—160°.

The phenomena of polymorphism are explained on the assumption that within the molecule as a whole there is a difference in the intensity of the energy between the different parts. Further, in consequence of these intramolecular differences there are variable external differences in intensity between similar molecules, so that the molecules become united in different ways. Thus two sodium acetate molecules may be united.

$$\begin{array}{ccc} \text{MeCO·ONa} & \text{MeCO—ONa} & \text{CH}_3\text{·CO·ONa} \\ \vdots & \vdots & \diagdown \\ \text{MeCO·ONa} & \text{CH}_3\text{·CO·ONa} & \text{NaO·CO·CH}_3. \end{array}$$
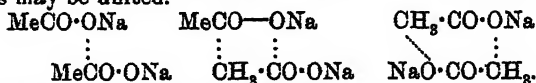
Such differences will explain the different crystalline structure of the polymorphic forms.　　　　　　　　　　　　　　　E. F. A.

The Solidifying- and Melting-points of Mixtures of Stearic and Oleic Acids. ROBERT MELDRUM (*Chem. News*, 1913, **108**, 199—201).—The investigation was undertaken to confirm the degree of accuracy of Dalican's method of determining the solidifying point and the thermometer bulb method of determining the melting point of mixtures of fatty acids.

In the first series of experiments, the solidifying points were taken in a test-tube 7 inches by 1 inch filled three parts full, which was suspended in a glass jar. The mixtures of acids were melted and cooled to within 10° of their solidifying point. The thermometer was inserted and when crystallisation had commenced the whole was very slowly stirred until the thermometer ceased to fall, when the latter was fixed in the centre, $1\frac{1}{2}$ inches from the bottom, and the readings completed. The point at which the thermometer rose and remained stationary was taken as the solidifying point. The method yields very concordant results for any given mixture and, contrary to the general belief, indicates the composition of the mixture more accurately when the solidifying point is low than when it is high.

A second series of experiments was performed in the same apparatus, but without stirring. The results are concordant among themselves, but both rise and solidifying point are lower than indicated by the first method. The rise appears to be rather erratic, and is apparently governed by the amount of matter crystallised per given interval of time. When working with large quantities, it appears to be eliminated.

A series of determinations of m. p. has also been made (1) by covering the thermometer bulb with a thin layer of substance, and suspending it inside a test-tube which is gradually heated in a beaker of water; (2) by the closed capillary tube method; (3) with an open capillary, and (4) with a capillary U-tube both limbs of which are left open. One limb contains a column of solid fat 4 cm. long. The tube is heated in a water-bath, the thermometer being placed between the limbs. The temperature at which both columns of fat are at equal height is taken as the m. p. The conclusion is drawn that the bulb method is the most accurate, the chief difficulty in it lying in obtaining a uniform coating of the fat. In the methods which depend on the displacement of the column of solid (Nos. 3 and 4), movement occurs before the latter is completely molten.　　　　　　　　H. W.

The Reaction between Acetoacetic Esters and Phenyl Iododichloride. GEORG SACHS (*Monatsh.*, 1913, **34**, 1409—1415).— The application of phenyl iododichloride as a chlorinating agent has been studied in the case of methyl and ethyl acetoacetates. Reaction with the methyl ester commenced at 34—35° and slackened after slightly more than one molecular proportion of phenyl iododichloride had been added at 60°. On distillation, a constant boiling, inseparable mixture of approximately two molecules of iodobenzene with one molecule of the expected methyl α-chloroacetoacetate, b. p. 84°/30 mm., was obtained. When ethyl acetoacetate was warmed at 60—80° with two molecules of the agent, however, iodobenzene, b. p. 79°/23 mm., and ethyl α-dichloroacetoacetate, b. p. 99°/21 mm., 207°/753 mm., were obtained.   J. C. W.

Optically Active Dimethylsuccinic Acid. ALFRED WERNER and M. BASYRIN (*Ber.*, 1913, **46**, 3229—3232).—It is shown that dimethylsuccinic acid may be resolved by means of optically active triethylenediaminecobaltic bromide. The modification of dimethylsuccinic acid, m. p. 195°, could not be resolved, and accordingly it represents the *meso*-form. The form m. p. 127° gives rise to d-*triethylenediaminecobaltic bromide* l-*dimethylsuccinate*, which is sparingly soluble, whereas the mother liquors contain the corresponding d-*dimethylsuccinate*. The optically active dimethylsuccinic acids have m. p. 135° and $[\alpha]_D$ +7·8° and −8·0.°   E. F. A.

Ketonic Decomposition of β-Lactones and its Application to the Synthesis of Ketens. ERWIN OTT (*Annalen*, 1913, **401**, 159—177).—Somewhat similar to the behaviour of dialkylmalonic anhydrides by heating, whereby dialkylketens are formed (Staudinger and Ott, A., 1908, i, 602), is the behaviour of derivatives of Meldrum's β-lactone of β-hydroxy*iso*propylmalonic acid (T., 1908, **93**, 601). In these also, by heating, the 4-ring is broken and acetone and ketens are obtained. The β-lactone of β-hydroxy*iso*-propylmalonic acid decomposes by heating into carbon dioxide, carbon suboxide, acetone, and acetic acid.

The β-*lactone* of β-*hydroxy-α-methyliso-propylmalonic acid*,

$$\begin{array}{c} O\!\!-\!\!CMe_2 \\ CO\cdot CMe\cdot CO_2H \end{array}'$$
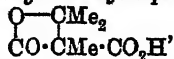
decomp. 110—113°, colourless leaflets, is obtained by treating methylmalonic acid with acetic anhydride and a little concentrated sulphuric acid, and keeping the product for many days with the calculated amount of acetone. The lactonic acid decomposes by heating into carbon dioxide, acetone, and viscous substances. It cannot be esterified directly, but the *methyl* ester, $C_8H_{12}O_4$, m. p. 59·5°, b. p. 71°/0·1 mm., is obtained, together with the β-lactones of β-hydroxy*iso*propylmalonic acid and of β-hydroxy-α-methyl*iso*propylmalonic acid, in a remarkable reaction between methyl iodide and the β-lactone of silver β-hydroxy*iso*propylmalonate. The methyl ester, which is remarkably stable and distils at 213°/723·4 mm., with only slight decomposition, yields, by heating in a current of hydrogen, carbon dioxide, acetone, and about 50% of dimethylketen.

The *β-lactone* of *a-bromo-β-hydroxyisopropylmalonic acid*,

$$\begin{array}{c} O—CMe_2 \\ | \\ CO \cdot CBr \cdot CO_2H \end{array}'$$
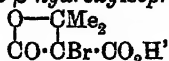
decomp. 87—92°, colourless needles, is prepared by exactly neutralising the β-lactone of β-hydroxy*iso*propylmalonic acid with 2N-sodium hydroxide in the cold and treating the solution slowly with the calculated amount of bromine. At 130° the brominated lactonic acid decomposes into acetone, carbon dioxide, and hydrogen bromide.

The *methyl* ester, $C_7H_9O_4Br$, m. p. 87°, colourless prisms, prepared from the silver salt and methyl iodide in benzene, is decomposed by slow distillation at 95° over a faintly glowing platinum spiral in a vacuum, whereby carbon dioxide, acetone, and *bromomethylketen*, $CBrMe:CO$, are obtained. Bromomethylketen is being fully examined; it polymerises with great readiness to a faintly yellow, resinous *substance*, $(C_3H_3OBr)_3$, m. p. 60—70°, and differs from all other ketens in not reacting with aniline.

Malonic acid and acetic anhydride in the presence of a little concentrated sulphuric acid yield, after removal of the excess of the anhydride and the acetic acid at 30—40°/1—2 mm., an extremely hygroscopic oil which is presumably the mixed malonic acetic anhydride, since it contains for each molecule of malonic acid, one acetyl group which cannot be removed without decomposition. The substance yields carbon suboxide by warming on the water-bath, and reacts with acetone to give an 87% yield of the β-lactone of β-hydroxy*iso*propylmalonic acid. Dimethylmalonic anhydride is obtained in 96% yield by treating dimethylmalonic acid with acetic anhydride and a little concentrated sulphuric acid, and removing by-products at 40°/1—2 mm., the operations being once repeated on the product. *Diethylmalonic anhydride*, prepared in a similar manner, is a liquid.   C. S.

Synthesis of Formaldehyde from Carbon Dioxide and Water by Inorganic Colloids acting as Transformers of Light Energy. BENJAMIN MOORE and T. ARTHUR WEBSTER (*Proc. Roy. Soc.*, 1913, [B], 87, 163—176).—The experiments of Bach, Euler, Usher, and Priestley (compare A., 1906, ii, 299, 881) have been confirmed and extended to show that formaldehyde is synthesised from carbon dioxide by means of inorganic colloidal uranic and ferric hydroxides in very dilute solution. The colloids act as catalysts for light energy, positive results being obtained only in strong, direct sunlight and in a "uviol" mercury arc. Under similar conditions, crystalloid uranium nitrate does not cause synthesis. The uranium catalyst is more powerful than the ferric catalyst. It is claimed that such a process occurring in nature forms the first step in the origin of life.
                                                    E. F. A.

Condensation of Aldol with Formaldehyde. V. P. KRAVEC (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1451—1453).—With the object of obtaining derivatives of pentaerythritol, from which the hydrocarbon, C_5H_8, regarded by Gustavson (A., 1896, i, 669) as vinyltrimethylene, has been obtained (compare Zelinski, this vol., i, 254), the author has investigated the condensation of aldol with formaldehyde under the

conditions laid down by Tollens and Wigand (A., 1892, 127); this reaction may be expected to give methylpentaerythritol.

Aldol may be readily prepared in good yield (30 grams) by a method devised by Zelinski and Volkonski, but not yet published. It consists in mixing acetaldehyde (100 grams), dissolved in an equal weight of water, with freshly precipitated, alkali-free lead hydroxide (30 grams) at a temperature not exceeding 5°, the mixture being left at the ordinary temperature for two hours and then gradually heated on the water-bath at 25°, 30°, and 35° during eighteen hours.

In presence of lead hydroxide, aldol and formaldehyde give pentaerythritol, so that resolution of the aldol molecule into 2 mols. of acetaldehyde precedes condensation with formaldehyde. The action of lead hydroxide on aldol is hence a typical, reversible reaction (compare de Bruyn and Alberda van Ekenstein, A., 1899, i, 850; Löb, A., 1909, i, 767; Löb and Pulvermacher, A., 1910, i, 95).

Pentaerythritol is also obtained from aldol and formaldehyde in presence of calcium hydroxide, but the latter is not able to effect the condensation of acetaldehyde to aldol.   T. H. P.

Mechanism of Oxidative Changes. HEINRICH WIELAND (*Ber.*, 1913, **46**, 3327—3342).—The catalytic action of palladium or platinum is not due to the activation of molecular oxygen with intermediate formation of peroxide, but it is attributed to the activation of hydrogen. This theory is extended to biological oxidations, and it is shown that certain of these can take place in presence of palladium black and in the complete absence of oxygen, provided that the accumulated hydrogen is removed by the presence of other substances with an affinity for hydrogen such as *p*-benzoquinone or methylene-blue.

Dextrose can be dehydrogenated by shaking with palladium black at 40° in an atmosphere of nitrogen, carbon dioxide being formed from the beginning of the reaction as well as hydrogen. The change is accelerated on the addition of *p*-benzoquinone, which is converted into quinhydrone or of methylene-blue, which is decolorised. In presence of oxygen which forms water with the liberated hydrogen, the change is still more rapid. Gluconic acid is even more quickly dehydrogenated.

Lactic acid yields pyruvic acid under similar conditions. Phenol, *m*-cresol, guaiacol, pyrogallol and aniline can be dehydrogenated in the absence of oxygen. Tyrosine and uric acid are resistant, but in both these cases the action of the oxydase is known to be combined with that of a hydrolysing enzyme.

Alcohol in presence of methylene-blue or of *p*-benzoquinone is converted into acetic acid by an acetone preparation of acetic acid bacteria, all oxygen being excluded. Acetaldehyde behaves similarly, whereas methyl alcohol or formaldehyde are converted into formic acid. Dextrose is dehydrogenated by the acetic acid ferment in presence of methylene-blue, carbon dioxide being formed.

The reducing enzymes, for example, Schardinger's reductase, act in the same manner. Salicylaldehyde is converted into salicylic acid by the milk enzyme either in presence of oxygen or in presence of methylene-blue in the absence of oxygen.   E. F. A.

Biochemical Synthesis of a Sugar of the Hexobiose Group, Gentiobiose. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and J. COIRRE (*Compt. rend.*, 1913, **157**, 732—734; *J. Pharm. Chim.*, 1913, [vii], **8**, 441—449).—The authors have prepared and isolated gentiobiose in a pure state by the action of emulsin, from almonds, on a concentrated solution of dextrose at 15—20° for one month. The excess of dextrose was removed by fermenting it with top yeast, after destroying the emulsin by heat and diluting the solution. The fermented liquid was neutralised with calcium carbonate, filtered and evaporated to dryness under reduced pressure. The dry residue was extracted with 95% alcohol, from which extracts two crops of crystals were obtained, the first containing mineral matter, and the second being pure gentiobiose as shown by its physical and chemical properties. W. G.

Peculiarity in the Solubility Curve of Sugar in Water. PH. ORTH (*Bull.* Assoc. chim. Sucr. Dist., 1913, **31**, 94—103).—A theoretical paper. It is shown that the equation $S = 28162/(157\cdot97 - t)$ gives the solubility of sucrose in water at a temperature t. The coefficient of supersaturation C_1 is obtained by the expression $C_1 = S(157\cdot97 - t_1)/28162$, in which S is the solubility at a temperature t and t_1, the lower temperature to which the solution is cooled without crystallisation. The constant $157\cdot97$ is shown to represent the temperature at which the solubility of sucrose in water becomes infinitely large, that is, the temperature at which sucrose and water are miscible in all proportions. A number of other empirical equations are given dealing with the freezing-point constant and the specific heat of aqueous solutions of sucrose, and also with the heat of solution.

J. F. S.

The Nitration of Cellulose, and the Decomposition of Nitrocellulose by Acids and Alkalis. G. MEISSNER (*Zeitsch. ges. Schiess. Sprengstoffwesen*, 1913, **8**, 252—254, 269—271).—An account of numerous experiments on the yields, stability, and variations in the products obtained by nitrating cellulose under different conditions, together with an account of the decomposition of these compounds by acids and alkalis. F. M. G. M.

Unstable Products in the Nitration of Cellulose. ERNST BERL and MAX DELPY (*Zeitsch. ges. Schiess. Sprengstoffwesen*, 1913, **8**, 129).—When water is removed from nitrocellulose by systematic treatment with alcohol, it gives rise to a brown powder, decomp. 162°, soluble in concentrated sulphuric acid; this when extracted with ether furnishes two *compounds*: (1) a yellowish-brown powder, decomposing at 174°, containing about 10% of nitrogen, and converted by concentrated alkalis into a compound soluble in water; and (2) a violet powder containing 9·45% of nitrogen and decomposing at 157°.

F. M. G. M.

Fatty Acid Esters of Hydrocellulose and their Hydrolysis. ALBRECHT STEIN (*Zeitsch. angew. Chem.*, 1913, **26**, 673—677).— Triacyl derivatives of hydrocellulose are prepared without difficulty by

acting on hydrocellulose with the anhydride of a fatty acid in the presence of concentrated sulphuric acid. The properties of the hydrocellulose esters of the homologues of acetic acid are similar to those of acetyl cellulose.

In order to obtain information as to the manner in which the catalyst acts in the esterification of hydrocellulose, the action of an acid anhydride on hydrocellulose in the presence of chloroacetic acid or trichloroacetic acid has been studied. It is found that the use of these catalysts leads to the production of an ester containing chlorine, in some cases to the extent of 2·8%.   W. H. G.

The Preparation of Triethylamine. JITENDRA NATH RAKSHIT (*J. Amer. Chem. Soc.*, 1913, **35**, 1781—1783).—If 75 c.c. of ethyl bromide and 50 c.c. of ammonia solution (D 0·88) are heated together in a closed 750 c.c. flask in the steam-oven for three hours, subsequent distillation with sodium hydroxide solution into dilute hydrochloric acid gives a mixture of ammonium chloride and ethylamine hydrochloride which are most easily separated by filtering the latter in a molten condition from the solid ammonium chloride.

The ethylamine from 62 grams of the hydrochloride is then mixed with 44 c.c. of ethyl bromide and again heated in a closed flask for three hours in the steam-oven. After cooling, the liquid is decanted from the separated crystalline solid and is then evaporated with dilute hydrochloric acid, when the residue (approximately 19 grams) consists of pure triethylamine hydrochloride.   D. F. T.

Resolution of α-Alanine into its Optical Antipodes by means of Active Acids. II. AMEDEO COLOMBANO and GIUSEPPE SANNA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 292—298. Compare this vol., i, 1208).—In alcoholic solution, the ethyl ester of alanine and *d*-camphorsulphonic acid yield the *salt* of the *inactive* ester,

$$CO_2Et \cdot CHMe \cdot NH_2, C_{10}H_{15}O \cdot SO_3H, \tfrac{1}{2}H_2O,$$
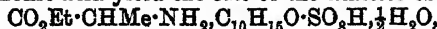
m. p. 95—100°, $[α]_D +11\cdot49°$. When water is used as solvent, crystalline fractions are obtained of gradually increasing melting point and specific rotation, but separation of the *d*- and *l*-alanines in this way is not easy.

Such resolution is, however, readily effected by means of *d*-bromocamphorsulphonic acid, mixing of the ammonium salt of this acid with alanine ester hydrochloride in aqueous solution resulting in the separation of *ethyl* d-*alanine* d-*bromocamphorsulphonate*,

$$CO_2Et \cdot CHMe \cdot NH_2, C_{10}H_{14}OBr \cdot SO_3H, 1H_2O,$$
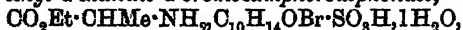
m. p. 145° or 192° (anhydrous), $[α]_D^{25} +67\cdot54°$ (hydrate), which corresponds with the dextro-ester and with *l*-alanine. Isolation of ethyl *l*-alanine *d*-bromocamphorsulphonate from the mother liquor is troublesome and gives only a small yield; possibly this ester could be more readily obtained by the use of *l*-bromocamphorsulphonic acid.
                                    T. H. P.

Tetra-aminoadipic Acid and αδ-Dihydroxy-βγ-diaminoadipic Acid. WILHELM TRAUBE and ARTHUR LAZAR (*Ber.*, 1913, **46**, 3438—3450. Compare A., 1903, i, 76).—An account of the replacement of the bromine atoms in the monolactam of αδ-dibromo-βγ-di-

aminobutane-$aa\delta\delta$-tetracarboxylic acid (1) and the dilactam of $a\delta$-dibromo-$\beta\gamma$-diaminoadipic acid (II) by the hydroxyl amino-, and dimethylamino-groups :

(I.) $CBr(CO_2H)_2 \cdot CH \underset{NH-\!-\!-CO}{\overset{CH(NH_2)}{<}} \!\!> CBr \cdot CO_2H$

(II.) $CO \underset{NH-\!-CH \cdot CHBr}{\overset{CHBr \cdot CH-\!-NH}{<}} \!\!> CO.$
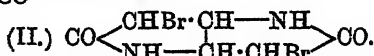
When heated at 105° with alcoholic ammonia, the dilactam of dibromodiaminoadipic acid is converted into the *dilactam* of *$a\beta\gamma\delta$-tetra-amino-adipic acid*, $CO \underset{CH(NH_2) \cdot CH-\!-\!-NH}{\overset{NH-\!-\!-CH \cdot CH(NH_2)}{<}} \!\!> CO$, which crystallises in stellar aggregates of short, stout needles, and forms a sparingly soluble *sulphate*, B,H_2SO_4 (solubility in water at 100° = 0·177 : 100), a *nitrate* (leaflets), *platinichloride* (hexagonal pyramids or rhombohedra), *hydrochloride* (colourless, prismatic needles), and *picrate* (fern-like aggregates).

The hydrochloride reacts with potassium cyanate in hot aqueous solution, yielding the *dilactam* of *$\beta\gamma$-diamino-$a\delta$-dicarbamidoadipic acid*, $C_8H_{12}O_4N_6$, which crystallises with water (1 mol.) in colourless needles.

Attempts to prepare tetra-aminoadipic acid by acidifying solutions of the dilactam in aqueous alkalis were unsuccessful, the original dilactam being precipitated unchanged.

The *dilactam* of *a-bromo-$\beta\gamma\delta$-triamino-a(or δ)carboxyadipic [a-bromo-$\beta\gamma\delta$-triaminobutane-$a\gamma\gamma$(or $aa\gamma$)-tricarboxylic] acid*, $C_7H_8O_4N_3Br$, obtained in the form of its *ammonium* salt by the action of alcoholic ammonia at 80—90° on the monolactam of $a\delta$-dibromo-$\beta\gamma$-diamino-butane-$aa\delta\delta$-tetracarboxylic acid, crystallises with water ($1\frac{1}{2}$ mol.) in needles (decomp. 280°) and yields salts with both bases and acids ; the *silver* salt (slender, colourless needles), *barium* salt, and *hydrobromide* (prisms) are described. The position of the free carboxyl group has not yet been determined. When kept in contact with an excess of aqueous dimethylamine (45%) for four or five days at the ordinary temperature, the dilactam of $a\delta$-dibromo-$\beta\gamma$-diaminoadipic acid is converted into the *dilactam* of *$\beta\gamma$-diamino-$a\delta$-tetramethyl-diaminoadipic acid* (III), which is separated from the accompaning *3 : 4-diaminotetrahydrofuran-2 : 5-dicarboxylic acid* (IV) by taking advantage of the sparing solubility of the latter compound in water.

(III.) $CO \underset{CH(NMe_2)_2 \cdot CH-\!-\!-NH}{\overset{NH-\!-\!-CH \cdot CH(NMe_2)_2}{<}} \!\!> CO.$

(IV.) $\underset{NH_2 \cdot CH-\!-CH \cdot NH_2}{\overset{CO_2H \cdot CH \cdot O \cdot CH \cdot CO_2H}{}}$.
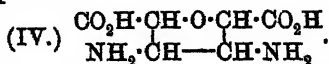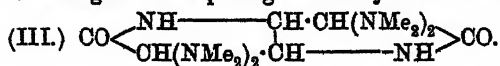
The furan compound crystallises in ill-defined tetragonal prisms which become yellow at 210°, and have m. p. 230° (decomp.). It forms with mineral acids very hygroscopic salts, of which the *nitrate* (decomp. 180°) is described. On treatment with fuming nitric acid, it yields *2-nitro-3 : 4-diaminofuran-5-carboxylic acid*, $C_5H_5O_5N_3$, crystallising in stellar aggregates of slender needles (decomp. above 300°). The dilactam, III, separates with $2H_2O$ in

well developed rhombic crystals, which darken at 243° and have m. p. 252° (decomp.). It forms a *hydrochloride*, $B,2HCl$, long, slender needles; a *picrate*, hexagonal leaflets; *platinichloride*, rectangular plates; *sulphate*, rhombic prisms, and an *oxalate*, prismatic needles.

The monolactam of $a\delta$-dibromo-$\beta\gamma$-diaminobutane-$aa\delta\delta$-tetracarboxylic acid reacts with silver nitrate in aqueous solution, yielding the *silver* salt, $C_8H_6O_7N_2Br_2Ag_2$, which is converted by boiling with water into the *monolactam* of $\beta\gamma$-*diamino*-$a\delta$-*dihydroxybutane* $aa\delta\delta$-*tetracarboxylic acid*, $OH \cdot C(CO_2H)_2 \cdot CH {<}{\begin{smallmatrix} CH(NH_2) \\ NH{-}CO \end{smallmatrix}}{>} C(OH) \cdot CO_2H$. The latter compound could not be obtained crystalline, and, therefore, was isolated in the form of its *silver* salt, $C_8H_9O_9N_2Ag$.

When heated either alone at 180° or in aqueous solution, it loses carbon dioxide and water, yielding the *dilactam* of $\beta\gamma$-*diamino*-$a\delta$-*dihydroxyadipic acid*, $CO {<}{\begin{smallmatrix} CH(OH) \cdot CH{-}{-}{-}NH \\ NH{-}{-}{-}CH \cdot CH(OH) \end{smallmatrix}}{>} CO$, which crystallises in tetragonal prisms capped with pyramids.

Attempts to prepare tetrahydroxyadipic acid from the dilactams of tetra-aminoadipic and $a\delta$-dihydroxy-$\beta\gamma$-diaminoadipic acids proved unsuccessful, the amino-groups in these compounds being stable towards the action of nitrous acid. F. B.

Preparation of Acetamide. E. F. HITCH and H. N. GILBERT (*J. Amer. Chem. Soc.*, 1913, **35**, 1780—1781).—Acetamide is conveniently prepared by heating a mixture of 42 grams of ammonium carbonate and 125 grams of acetic acid (compare Rosanoff, Gulick, and Larkin, A., 1911, i, 529) in a 250 c.c. round-bottomed flask in an air-bath. The flask is fitted with a Vigreux fractionating column carrying a thermometer and attached to a condenser. The mixture is boiled at such a rate that 20 to 30 drops distil per minute, and when the thermometer registers 223° the residue in the flask is almost pure acetamide.

The yield is 85—90% calculated on the ammonium carbonate, and the time required is four hours. D. F. T.

Synthesis of Amido-oxalylbiuret. JOHAN TH. BORNWATER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 198—200).—In a previous paper (A., 1911, i, 617) the author has shown that finely-powdered carbamide reacts with an ethereal solution of oxalyl chloride, yielding parabanic acid and, apparently, oxalyldiureide,

$$C_2O_2(NH \cdot CO \cdot NH_2)_2,$$
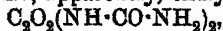
which is quite different from Grimaux's compound (A., 1880, 105) obtained by fusion of a mixture of carbamide and parabanic acid. Subsequently, the subject has been re-investigated by Biltz and Topp (this vol., i, 600, 602), who are led to the conclusion that the two substances are probably identical, although certain differences remain unexplained. The author points out that Grimaux's compound has been incorrectly described as oxalyldiureide in the German literature, since Grimaux calls it, "amide d'un acide oxalylbiurétique." He has further effected the synthesis of the latter compound.

Carbethoxyethoxalylcarbamide, $CO_2Et \cdot NH \cdot CO \cdot NH \cdot CO \cdot CO_2Et$, needles, m. p. 152°, is obtained in 10% yield when ethyl oxamate and ethyl urethane are heated in dry benzene. When a solution of this substance in absolute alcohol is treated with dry, gaseous ammonia, amido-oxalylbiuret, $NH_2 \cdot CO \cdot CO \cdot NH \cdot CO \cdot NH \cdot CO \cdot NH_2$, is precipitated, which is identical with Grimaux's compound.

In effecting the biuret reaction, the author points out the desirability of first adding the highly diluted copper sulphate solution, and, subsequently, a solution containing at most 15% of potassium hydroxide. When the reagents are added in the reverse order and more concentrated solutions of potassium hydroxide are employed (compare Biltz and Topp, *loc. cit.*), there is a possibility that the substance is already undergoing partial decomposition before the copper sulphate is added.

The substance, $C_4H_5O_3N_3$, m. p. 272—273° (decomp.), obtained by the action of fuming hydriodic acid (D 1·96) on Grimaux's compound, is, possibly, uramil, the formation of which is explicable on the author's formulation of Grimaux's compound. H. W.

Simultaneous Reduction and Oxidation. I. Dichloropyruvic Acid, Nitrile and Ester from Trichlorolactic Acid, Nitrile and Ester. ARTHUR KÖTZ and K. OTTO (*J. pr. Chem.*, 1913, [ii], **88**, 531—552. Compare Wallach, this Journ., 1875, 351; A., 1878, 285, 288; Pinner, this Journ., 1877, ii, 584; A., 1884, 1298). —With the object of throwing further light on the mechanism of the transformation of chloral into dichloroacetic acid under the influence of aqueous potassium cyanide, the authors have undertaken a systematic examination of similar cases of simultaneous reduction and oxidation occurring in compounds of the type $CCl_3 \cdot CH(OH) \cdot R$, the present paper dealing particularly with the transformation of $\beta\beta\beta$-trichlorolactic acid, and its nitrile and ester into the corresponding derivatives of dichloropyruvic acid.

They consider that the first stage in the reaction between chloral and potassium cyanide consists in the formation of $\beta\beta\beta$-trichloro-lactonitrile (I), and that this loses hydrogen chloride, yielding the compounds (II) or (III), which are at once transformed into dichloro-pyruvonitrile (IV), the latter compound then undergoing hydrolysis to dichloroacetic and hydrocyanic acids:

(I) $CCl_3 \cdot CH(OH) \cdot CN \longrightarrow$ (II) $CCl_2{:}C(OH) \cdot CN$, or

(III) $\overset{\displaystyle\frown}{CCl_2 \cdot CH} \cdot CN \longrightarrow$ (IV) $CHCl_2 \cdot CO \cdot CN \longrightarrow CHCl_2 \cdot CO \cdot OH + HCN.$
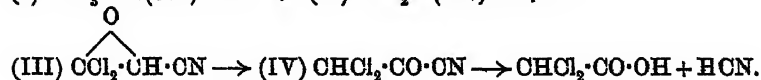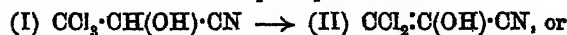
The following evidence is given in support of the view that $\beta\beta\beta$-trichlorolactonitrile is intermediately formed in the reaction: (1) Although potassium cyanide is hydrolysed to potassium hydroxide and hydrogen cyanide, the action of potassium cyanide on chloral does not give rise to chloroform, and therefore the chloral cannot be present as such in the mixture. (2) $\beta\beta\beta$-Trichlorolactonitrile, on treatment with potassium hydroxide, gives rise to potassium dichloroacetate, no chloroform being produced in the reaction.

$\beta\beta\beta$-Trichlorolactonitrile thus differs from chloral in not undergoing hydrolysis with the formation of chloroform. This difference is referred by the authors to the reactivating influence of the cyanogen group on the hydrogen atom directly attached to the central carbon of the nitrile; on account of this mobility of the hydrogen atom, the molecule readily loses hydrogen chloride, whilst at the same time the ability to yield chloroform by hydrolysis disappears.

A similar difference is shown by $\beta\beta\beta$-trichloroethyl alcohol, ethyl $\beta\beta\beta$-trichlorolactate, and other compounds of the type

$$CCl_3 \cdot CH(OH) \cdot R.$$
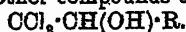
On treatment with triethylamine, ethyl $\beta\beta\beta$-trichlorolactate and $\beta\beta\beta$-trichlorolactonitrile lose hydrogen chloride, yielding ethyl dichloropyruvate and dichloropyruvonitrile. The last-mentioned compound reacts with water and alcohol, yielding dichloroacetic acid and ethyl dichloroacetate.

The formation of dichloroacetamide, dichloroacetanilide, and ethyl dichloroacetate by the action of ammonia, aniline and alcohol on $\beta\beta\beta$-trichlorolactonitrile (Pinner and Wallach, *loc. cit.*) is considered by the authors to furnish additional support to their view that dichloropyruvonitrile is formed as an intermediate product in the action of potassium cyanide on chloral.

When heated with water or triethylamine, trichlorolactic acid decomposes, thus: $CCl_3 \cdot CH(OH) \cdot CO_2H \longrightarrow HCl + CHCl_2 \cdot CO \cdot CO_2H \longrightarrow CO_2 + CHCl_2 \cdot CHO.$

The readiness with which this decomposition takes place affords an explanation of the fact that the interaction of trichlorolactic acid and ammonia, hydroxylamine, phenylhydrazine, or carbamide gives rise to derivatives of glyoxal or dichloroacetaldehyde.

Dichloropyruvonitrile is obtained (1) by the interaction of molecular proportions of trichlorolactonitrile and triethylamine in ethereal solution at the ordinary temperature, and (2) by heating dichloroacetyl chloride with silver cyanide. It forms a colourless liquid, b. p. 111—113°/12 mm.

$\beta\beta$-Dichloro-a-benzyliminopropiobenzylamide,

$$CHCl_2 \cdot C(:N \cdot C_7H_7) \cdot CO \cdot NH \cdot C_7H_7,$$
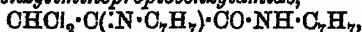
prepared by heating ethyl trichlorolactate with benzylamine (3 mols.) in ethereal solution, crystallises with water (1 mol.) and has m. p. 101° (not sharp). It may also be obtained by heating ethyl dichloropyruvate with benzylamine (2 mols.) in ethereal solution. When prepared by the second method, it crystallises with $2H_2O$ in lustrous, white leaflets, m. p. 220—221°, or slender needles, m. p. 104° and 150°.

Ethyl dichloropyruvate, prepared by heating ethyl trichlorolactate and triethylamine in alcoholic solution, is a colourless liquid, b. p. 115°/12 mm. It rapidly takes up water on exposure to air, and then has the composition $C_5H_6O_3Cl_2, 2H_2O$.

Dichloropyruvic acid, $C_3H_2O_3Cl_2, H_2O$, obtained by hydrolysing the ester with hydrochloric acid, separates from a mixture of ether and light petroleum in white crystals, m. p. 119°, b. p. 215—220°, and after distillation has m. p. 110°. When boiled with water, it is converted into dichloroacetaldehyde.   F. B.

Nitrogen Carbides. HERMANN PAULY and ERNST WALTZINGER (*Ber.*, 1913, **46**, 3129—3140).—It has already been shown (A., 1910, i, 639) that tetraiodoglyoxaline decomposes on heating to form the compounds C_8N_3I and then C_8N_2, the reaction recalling the formation of paracyanogen from cyanuric iodide (Klason, 1886, 1001). The fact that the decomposition takes place at a temperature which, according to experience, is not inimicable to the glyoxaline ring, suggests that the compounds formed still have ring structure, since a partial loss of nitrogen might be expected to ensue if the ring were opened. In order to test this point, and also to learn whether the preliminary decomposition into a monoiodo-compound was general, tri-iodo-5- and 2-methylglyoxalines and tetraiodopyrrole (iodole) have also been heated. In these cases, however, the compounds melt and enclose some of the liberated iodine, so that the formation of intermediate compounds was masked, and, in addition, the presence of hydrogen was disturbing and led to the production of a little ammonium iodide,

All the compounds obtained, C_8N_2, C_8N_2Me and C_4NH, are amorphous, charcoal-like products, and have, in common with paracyanogen, the following properties : they yield cyanogen on heating to redness in an indifferent atmosphere ; they give up all their nitrogen as ammonia when heated with soda-lime ; they dissolve in molten alkalis, forming ammonia, cyanides and carbonates. Animal charcoal has some of these properties, but does not dissolve in molten alkali. It may consist in part of such nitrogen carbides.

Quantitative studies on the decomposition of tetraiodoglyoxaline were carried out in a glass tube which was slightly bent downwards, so that it dipped below the surface of a metal bath. One end of the tube was attached to a U-tube and a flask containing potassium iodide solution for the absorption of iodine. The iodine was swept out by a stream of carbon dioxide. Since the tetraiodoglyoxaline cannot be purified by recrystallisation, it was analysed before use. It was found that, however carefully prepared, it contained about 1% of a by-product which could be removed by volatilisation at 105° in vacuum. The carbides obtained, readily absorbed gases and moisture, so that all analytical processes were carried out with the greatest expedition.

The formation of the soot-like, sepia-coloured *iodo-nitrogen carbide*, $(C_8N_2I)_x$, takes place at 180°. The substance forms a brown solution in nitric acid, iodine being liberated. The *carbide*, $(C_8N_2)_x$ is best obtained by heating tetraiodoglyoxaline, first at 180° and then at 420°. When heated at 800—900° in a current of carbon dioxide, cyanogen and a little carbon monoxide were formed, but in an atmosphere of nitrogen, the formation of cyanogen was quantitative. J. C. W.

Iron Salts which Combine with Carbon Monoxide. II. The Action of Amines on Sodium Nitroprusside. WILHELM MANCHOT and PIERRE WORINGER (*Ber.*, 1913, **46**, 3514—3521).—It has been shown previously (A., 1912, i, 955) that the action of ammonia on sodium nitroprusside is expressed by the equation :

$$Na_2[Fe(CN)_5NO] + 3NH_3 + H_2O =$$
$$Na_2(NH_4)[Fe(CN)_5,NH_3] + NH_4 \cdot NO_2.$$
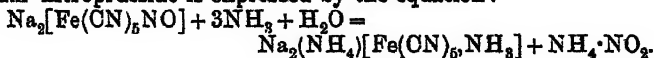
It has now been found possible to replace the NO-group by alkyl-amines instead of ammonia, and the compounds thus formed give similar reactions to the ammonia compound, and also possess the property of combining with carbon monoxide and oxygen. Methyl-amine, dimethylamine, trimethylamine, and ethylenediamine react very readily, but aromatic amines, such as aniline, toluidine, etc., have no action on sodium nitroprusside.

Trisodium ferropentacyanomethylamine, $Na_3[Fe(CN)_5, NH_2Me]$, was obtained in the form of yellow crystals from sodium nitroprusside and methylamine in aqueous methyl-alcoholic solution, dilution with the alcohol being necessary to moderate the reaction. The reaction mixture also contained sodium acetate, to prevent the formation of a disodium methylamine salt.

The *disodium ethylenediamineferropentacyanoethylenediamine*,
$$Na_2[Fe(CN)_5], C_2H_4(NH_2)_2,$$
was not obtained pure, although the product was well crystallised, and appeared homogeneous under the microscope. The addition of sodium acetate to the reaction mixture did not give a trisodium salt.

Although sodium nitroprusside does not react with pyridine, the salt *trisodium ferropentacyanopyridine*, $Na_3[Fe(CN)_5, C_5H_5N]$, can be obtained by the action of pyridine on an aqueous-methyl alcoholic solution of trisodium ammonium ferropentacyanoammine. It crystal-lises as a felted mass of long, yellow needles, and possesses properties similar to those of the alkylamine compounds.

Experiments to prepare the ferric compounds corresponding with the ferropentacyanocarbon monoxide salts have not hitherto been successful.   T. S. P.

Action of Organomagnesium Compounds on Ethyl Diazo-acetate. ERNST ZERNER (*Monatsh.*, 1913, 34, 1609—1630).—By means of the reaction between organomagnesium compounds and ethyl diazoacetate or diazomethane, the author hoped to be able to throw some light on the constitution of aliphatic diazo-compounds. No direct proof of the ring or open-chain structure could be obtained, but the results offer more support to the latter view than to the former. The author crities the Angeli-Thiele formula, $R:N:N$, however, and proposes instead the type $R:N\cdot N$, making the active nitrogen atom univalent.

Although Thiele has suggested that certain reactions of nitrous oxide agree with the constitution $O:N:N$, it was found that the gas has no action whatever on magnesium methyl iodide. When ethyl diazotate was added to magnesium methyl iodide at $0°$, however, a vigorous reaction occurred, and a crystalline solid and an oil were obtained. The former was most probably the *methylhydrazone* of *ethyl glyoxylate*, $CO_2Et\cdot CH:N\cdot NHMe$. It formed long, colourless needles, m. p. 91—92°, responded to Molisch's thymol reaction and Tollens's naphtharesorcinol test, and reduced ammoniacal silver and Fehling's solutions. It was hydrolysed by warm dilute sulphuric acid, and methylhydrazine sulphate and ethyl glyoxalate were obtained. An *acetyl* derivative, $C_7H_{12}O_3N_2$, was also prepared, in freely soluble white needles, m. p. 67—69°. The oily product also gave methyl-

hydrazine on hydrolysis. It was probably impure methylhydrazone of hydroxy*iso*butaldehyde, $OH \cdot CMe_2 \cdot CH:N \cdot NHMe$. The crystalline compound might also have been ethyl N-methylhydraziacetate,

$$CO_2Et \cdot CH \big\langle{}^{NH}_{NMe}\text{,}$$ but this would assume that the diazo-compound reacts differently from the fatty azoimides, which, under the influence of organomagnesium haloids, yield fatty diazoamino-compounds, as Dimroth has shown.

To elucidate this point the action of ethyl diazoacetate on magnesium phenyl bromide was investigated, since it was expected that either the known phenylhydrazone of ethyl glyoxylate or an isomeride would be obtained. However, the only crystalline product was one in which the ester group had also been attacked. It was most probably the *phenylhydrazone* of *hydroxydiphenylacetaldehyde*, $OH \cdot CPh_2 \cdot CH:N \cdot NHPh$. It crystallised in large, rectangular plates, m. p. 132°, and yielded a red, crystalline *product*, $C_{20}H_{16}N_2$, m. p. 69—70°, on boiling with dilute sulphuric acid, water being eliminated. The red compound gave intense, red solutions in concentrated mineral acids. On evaporating the solution in hydrochloric acid in a desiccator over lime, a snow-white, additive *product*, $C_{20}H_{17}N_2Cl$, was obtained. This was very sparingly soluble in water, but gave a turbidity with silver nitrate. It was freely soluble in organic media, and exhibited a fine blue fluorescence in alcohol. Here again the crystalline product might have been the hydrazi-compound,

$$OH \cdot CPh_2 \cdot CH \big\langle{}^{NPh}_{NH}\text{,}$$ but this did not give a condensation product with any chromophoric groups.

Magnesium ethyl iodide and ethyl diazoacetate were also brought together, and ethylhydrazine sulphate was obtained by hydrolysing the unpleasant smelling, brown syrup which resulted.

When diazomethane was distilled into magnesium benzyl chloride, an oily product which contained crystals of either the benzylhydrazone of formaldehyde, or benzylhydrazimethylene, was obtained. The *compound*, $C_8H_{10}N_2$, formed stable, white plates, m. p. 124°, whereas a crystalline product obtained by mixing 40% formaldehyde and benzylhydrazine was very unstable.　　　　　　　　J. C. W.

Organic Silicon Compounds which Liberate Hydrogen from Silicon Hexachloride and Magnesium Methyl Bromide or Iodide. GEOFFREY MARTIN (*Ber.*, 1913, **46**, 3289—3295. Compare this vol., i, 961).—By the action of magnesium methyl bromide on silicon hexachloride, a compound, $Si_6H_6O_{12}Me_2$, is obtained, which yields 102—118 c.c. of hydrogen per gram of substance when decomposed with potassium hydroxide. Under other experimental conditions, compounds $Si_6H_4O_{12}Me_4$, $Si_6HO_{11}Me_5$, and $Si_6H_2O_7Me_8$ are obtained; these yield less and less hydrogen on decomposition as the number of methyl groups increases.

Hexamethylsilicoethane, Si_2Me_6 (Bygden, A., 1912, i, 341), does not yield hydrogen on decomposition, although containing the linking Si—Si. Evidently the characteristic decomposition of silicon

compounds with alkali hydroxide is due to the association of oxygen complexes with the silicon atoms.   E. F. A.

The Isolation and Properties of Some Electropositive Groups and their Bearing on the Problem of the Metallic State. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1913, **35**, 1732—1741).—When solutions of mercury alkyl salts in liquid ammonia are electrolysed, the free mercury alkyl group is deposited at the cathode, except in the case of members of the series above C_4H_9Hg, when no deposition takes place. The electrolytic cell used contained small platinum wires as electrodes, the cathode being situated at the bottom of the cell. The free groups deposited as an attenuated, opaque mass, which, by means of pressure, could be brought into a fairly coherent form. They are good conductors of electricity and do not amalgamate with mercury to any extent.

The *mercury methyl group*, $HgCH_3$, was obtained pure from the compound MeHgCl by washing it free from salt with liquid ammonia. Decomposition takes place at ordinary temperatures, with the formation of mercury and mercury methyl, $HgMe_2$; there is appreciable decomposition at $-33°$. The ethyl derivative behaves similarly, but the propyl derivative is less stable. The ethyl mercury group, when compressed, exhibits metallic reflection of a copper colour, whereas the mercury methyl group is black.

Attempts to isolate groups by the electrolysis of liquid ammonia solutions of the following salts were not successful : Me_4SbI, Me_3SI, Ph_2II, $C_5H_{11}HgI$, $C_8H_{17}HgI$, PhHgI, and Me_3SnI.

The bearing of the above results on the metallic state is discussed, and the conclusion drawn that the electrons to which conduction is due in metals are the same electrons which are involved in the common chemical combination of metals with other elements.   T. S. P.

The Optical Activity of Petroleum and its Significance. FRANK W. BUSHONG (*Science*, 1913, **38**, 39—44).—Attention is drawn to the optical activity of the heavy oils. Since the naphthenic acids derived from the petroleum by treatment with alkali during refining are optically active, the activity of the original oil might be attributed to these acids. It does not necessarily follow, however, that the optically active constituents present in these naphthenic acids are identical with those originally present in the petroleum, and there seems good evidence that this is not the case, as both the author and others have found that the heavy oils retain most of their optical activity after treatment with alcoholic potash ; still, the optical activity may be due to some extent to these acids. It is probable that the oils contain active hydrocarbons (naphthenes), and it is generally held that the naphthenic acids are oxidation products of these.

[The author's views as to the cause of the activity of petroleum were somewhat misrepresented in an earlier abstract (this vol., i, 969).]   J. C. W.

Distillation of Coal under Reduced Pressure. AMÉ PICTET and MAURICE BOUVIER (*Ber.*, 1913, **46**, 3342—3353 ; *Compt. rend.*, 1913, **157**, 779—781).—In an earlier paper (Pictet and Ramseyer, A., 1911, i, 850) it has been shown that extraction of coal (Montrambert) with boiling benzene gives a mixture of hydroaromatic hydrocarbons, from which a hexahydrofluorene, $C_{13}H_{16}$, could be isolated ; it was also mentioned that distillation of the same coal under reduced pressure produced a similar mixture in which the same hydrocarbon could be detected. As the latter procedure was more rapid and gave better yields, it has now been applied more carefully.

The method was to heat 2—5 kilograms of the coal in a vertical iron retort of approximately 10 litres capacity ; the temperature was slowly raised to 450°, whilst the pressure was maintained at a few centimetres of mercury by means of water-pumps. The experiment generally occupied about five hours.

Of the products of the decomposition, the tar only was carefully investigated ; the gases were not collected, but were observed to resemble butadiene and isoprene in odour ; the water had an acid reaction and contained no ammonium salts ; the coke was found to yield still further quantities of combustible gas when heated more strongly. The tar, which amounted to approximately 4% of the coal, was lighter than water, had a brown colour with feeble green fluorescence, and resembled petroleum in odour ; it contained no phenols, but a considerable quantity of bases which appeared to be mainly of the secondary type. Careful fractionation under reduced pressure failed to disclose the presence of any solid substances, and oxidation yielded only aliphatic acids, indicating the absence of aromatic hydrocarbons. It is therefore probable that the tar is a mixture of hydroaromatic compounds of the naphthene class.

Decomposition of the crude tar by distillation at ordinary pressure through a red-hot iron tube packed with coke produced a considerable quantity of gas resembling coal gas in odour, and consisting mainly of hydrogen and paraffin hydrocarbons together with water containing much free ammonia and a dark-coloured tar resembling coal-tar in odour. This tar, unlike the original product, contained phenols, bases recalling the odour of pyridine, and aromatic hydrocarbons, amongst which benzene, naphthalene, and anthracene could be identified. It is tentatively suggested that in coal distillation the methane, ammonia, phenols, and aromatic hydrocarbons are not primary products, but are formed by the decomposition of intermediate products represented by the above " vacuum tar."

Treatment of certain fractions of the " vacuum tar" with sodium removes certain hydroxy-compounds (the presence of which had already been indicated by the results of analysis) which exhibit the usual behaviour of alcohols towards alkalis and acyl chlorides. The natural supposition that these alcohols form the origin of the phenolic substances during subsequent decomposition by further heat received no confirmation when they were passed in the vapourous condition through a red-hot tube, the only products being unsaturated hydrocarbons.

The hydrocarbon residues after extracting various fractions with

sodium immediately decolorise cold potassium permanganate solution, and consequently must contain unsaturated hydrocarbons. The latter were removed by the action of fuming sulphuric acid, and the residue again heated with sodium. By repeated fractional distillation the liquid was separated into various portions in the hope of identifying some of the constituents. Decahydronaphthalene was definitely proved to be absent, and a comparison of the compositions and densities of the various fractions with those of corresponding fractions from Caucasian petroleum clearly demonstrated their distinct character. A similar comparison with fractions from Canadian petroleum (which is also known to contain hydrocarbons of the general formula C_nH_{2n}) proved the identity of the fractions containing the hydrocarbons $C_{10}H_{20}$ and $C_{11}H_{22}$. The former of these is very sensitive to most reagents, and generally gives complex reaction products, but by the action of bromine vapour, dibromodurene (?), m. p. 202°, could be obtained; also by distillation over iron oxide at a dull red heat a distillate is obtained, which on nitration yields dinitrodurene (?), m. p. 202°. Although this evidence is not regarded as final, the authors consider themselves justified in identifying the hydrocarbon, $C_{10}H_{20}$, with hexahydrodurene (s-tetramethyl*cyclo*hexane), whilst to the hydrocarbon, $C_{11}H_{22}$, they ascribe the structure of a pentamethyl-*cyclo*hexane.   D. F. T.

Electrolytic Oxidation of Toluene. FRITZ FICHTER (*Zeitsch. Elektrochem.*, 1913, **19**, 781—784).—A suspension of toluene in 2N-sulphuric acid is placed in a large cylindrical lead vessel which serves as anode; a cathode consisting of a lead spiral is used. The suspension is vigorously stirred, and a current of 0·01 ampere per sq. cm. of anode is passed through until one-half of the toluene has disappeared. Stopping the process at this point, prevents the destruction of some of the products by further oxidation. The toluene layer on allowing it to settle contains after the oxidation toluquinone and a little benzaldehyde, whilst the aqueous layer contains quinol and phenol.

The process of the reaction proceeds as indicated :

$$CH_3 \cdot C_6H_5 \nearrow \begin{array}{l} HO \cdot C_6H_4 \cdot CH_3 \ (1:2) \longrightarrow \\ HO \cdot C_6H_4 \cdot CH_3 \ (1:4) \longrightarrow \\ C_6H_5 \cdot CHO \end{array}$$

$$(HO)_2C_6H_3 \cdot CH_3 \ (1:2:5) \longrightarrow CH_3 \cdot C_6H_3O_2$$
$$HO \cdot C_6H_3 \cdot CHO \ (1:4) \nearrow \begin{array}{l} C_6H_4(OH)_2 \ (1:4) \\ C_6H_5 \cdot OH \end{array}$$
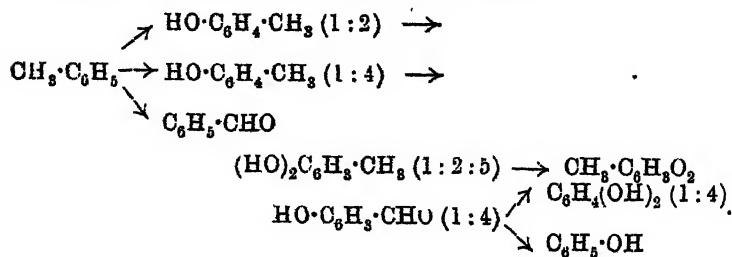
It is thus obvious that the oxidation occurs mainly in the nucleus (compare also T. Kempf, A., 1901, i, 728; R. Kempf, A., 1911, i, 464).   J. F. S

Transformations of Unsaturated Haloid Compounds. II. Cinnamaldehyde and Phenyl Vinyl Ketone. FRITZ STRAUS and ABRAHAM BERKOW (*Annalen*, 1913, **401**, 121—159. Compare Straus, A., 1912, i, 989).—It has been shown (*loc. cit.*) that the changes R·CO·CH:CHR′ —→ R·CH:CH·CO·R′ —→ R·CO·CH:CHR′ can be effected by a series of substitutive reactions. The present paper deals with a simple case in which R′ is hydrogen. The conversion of cinnamaldehyde into phenyl vinyl ketone has been accomplished, but the reverse change of the ketone to the aldehyde has revaled unexpected and important peculiarities.

Cinnamaldehyde and phosphorus pentachloride readily yield the normal keto-chloride, cinnamylidene dichloride (*loc. cit.*), an ethereal solution of which reacts with a slight excess (over 1 mol.) of sodium methoxide to form α-*chloro-γ-methoxy-γ-phenyl-Δ*ª*-propene*,

$$CHCl:CH·CHPh·OMe,$$
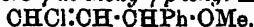
b. p. 111°/18 mm., D_4^{15} 1·0959. The latter is converted in petroleum solution in the presence of calcium chloride into cinnamylidene dichloride by hydrogen chloride, yields cinnamaldehyde by hydrolysis, and is oxidised to α-methoxyphenylacetic acid by potassium perman·ganate in acetone. α-*Chloro-γ-ethoxy-γ-phenyl·Δ*ª*-propene*, $C_{11}H_{13}OCl$, b. p. 120·5°/12 mm., is prepared similarly. An ethereal solution of cinnamylidene dichloride and N-sodium hydroxide (1½ mols.) yields after a hundred and twenty hours a substance which loses water by distillation in a vacuum, and is converted into γ-*chloro-α-phenylallyl ether*, $(CHCl:CH·CHPh)_2O$, b. p. 127°/18 mm.

The *acetal* of phenyl vinyl ketone, $CH_2:CH·CPh(OMe)_2$, b. p. 85—86°/12 mm., D_4^{15} 0·9887, is obtained by boiling α-chloro-γ-methoxy-γ-phenyl-Δª-propene with 5% methyl-alcoholic sodium methoxide (2 mols.) for four days. The constitution of the acetal is proved by reduction by colloidal palladium and hydrogen at 2 atmospheres, whereby the *acetal*, b. p. 206—208° or 92—93°/18 mm., of phenyl ethyl ketone is obtained. The hydrolysis of the unsaturated acetal to phenyl vinyl ketone is difficult on account of the instability of the ketone, and has only been effected by means of 5% sulphuric acid at 60—70° in the absence of light.

Phosphorus pentachloride (1½ mols.) reacts with phenyl vinyl ketone in benzene to form αγ-*dichloro-α-phenyl-Δ*ª*-propene*, $CPhCl:CH·CH_2Cl$, b. p. 124—125°/16 mm., the constitution of which is proved by the action of ozone, followed by that of water, on the substance in carbon tetrachloride, whereby, amongst other products, benzoic and chloroacetic acids are obtained. The substance reacts with a slight excess (over 1 mol.) of methyl-alcoholic sodium methoxide to form quantitatively α-*chloro-γ-methoxy-α-phenyl-Δ*ª*-propene*, $CPhCl:CH·CH_2·OMe$, b. p. 131—132°/27 mm., D_4^{22} 1·146, which is reconverted into αγ-dichloro-α-phenyl-Δª-propene by hydrogen chloride in petroleum in the presence of calcium chloride, and yields benzoic acid by oxidation in acetone with potassium permanganate. By reduction in acetone with colloidal palladium and hydrogen at 2 atmospheres, α-chloro-γ-methoxy-α-phenyl Δª-propene is converted into *methyl γ-phenylpropyl ether*,

$$CH_2Ph·CH_2·CH_2·OMe,$$
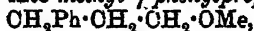
b. p. 207—208° or 92—94°/12 mm., D_4^{15} 0·9990, which has also been prepared from γ-phenylpropyl chloride and an excess of boiling 5% sodium methoxide ; *methyl α-phenylpropyl ether*, OMe·CHPhEt, prepared from α-phenylpropyl chloride in a similar manner, has b. p. 183—185° or 76—77°/14 mm., D_4^{15} 0·9216, and a quite different odour.

By boiling for four and a-half to five days with 5% sodium methoxide, α-chloro-γ-methoxy-α-phenyl-Δ^a-propene is converted, unexpectedly, into *αγ-dimethoxy-α-phenyl-Δ^a-propene*,

$$OMe·CPh:CH·CH_2·OMe,$$

b. p. 100—102°/11 mm., D_4^{17} 1 0412, which yields benzoic acid by oxidation in acetone by potassium permanganate, and is reduced by hydrogen and colloidal palladium to *αγ-dimethoxy-α-phenylpropane*, OMe·CHPh·CH$_2$·CH$_2$·OMe, b. p. 215—217° (decomp.) or 94—95°/ 15 mm., D_4^{10} 0·9829. The last substance has also been prepared from γ-chloro-α-phenylpropyl alcohol (Fourneau, A., 1907, i, 762); the chlorohydrin in benzene in the presence of calcium bromide is converted by hydrogen bromide into *γ-chloro-α-bromo-α-phenylpropane*, CHPhBr·CH$_2$·CH$_2$Cl, b. p. 118—120°/20 mm., which is converted by sodium methoxide successively into *γ-chloro-α-methoxy-α-phenylpropane*, $C_{10}H_{13}OCl$, b. p. 110—112°/12 mm., and αγ-dimethoxy-α-phenylpropane.   C. S.

p-Nitrophenylethyl Chloride [β-Chloro-4-nitroethylbenzene]. JULIUS VON BRAUN and B. BARTSCH (*Ber.*, 1913, **46**, 3050—3055).— The product obtained by nitrating β-chloroethylbenzene can be separated into two portions, of which one is solid, the other liquid. The former, which may constitute 50% of the mixture, has been shown to be β-chloro-4-nitroethylbenzene (A., 1912, i, 498). The latter is now shown to have a similar constitution, since, on nitration, each substance yields *β-chloro-2-nitro-4-aminoethylbenzene*, which can be further reduced to *β-chloro-2 : 4-diaminoethylbenzene*, whilst, under the influence of sodium acetate and glacial acetic acid, each substance is transformed into a mixture of *4-nitro-β-acetoxyethylbenzene*, NO$_2$·C$_6$H$_4$·CH$_2$·CH$_2$·OAc and *4-nitro-α-acetoxyethylbenzene*,

$$NO_2·C_6H_4·CHMe·OAc,$$
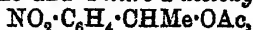
from which, on saponification, the corresponding alcohols are obtained. The formation of the latter substance probably depends on the intermediate production of 4-nitrostyrene, NO$_2$·C$_6$H$_4$·CH:CH$_2$. A similar reaction is not observed to any extent with β-chloroethylbenzene or γ-chloronitropropylbenzene.

β-Chloro-2-nitro-4-aminoethylbenzene, m. p. 84°, is obtained by the action of nitric and sulphuric acids on the hydrochloride of β-chloro-4-aminoethylbenzene obtained from solid β-chloro-4-nitroethylbenzene (compare A., 1912, i, 498). The *hydrochloride*, m. p. 190°, and the *benzoyl* derivative, m. p. 130°, have been prepared. Identical products are obtained from liquid β-chloro-4-nitroethylbenzene. Reduction of β-chloro-2-nitro-4-aminoethylbenzene (whether obtained from solid or liquid β-chloro-4-nitroethylbenzene) by means of stannous chloride gives *β-chloro-2 : 4-diaminoethylbenzene hydrochloride*, m. p. 256°, after darkening at 250°. The colour reactions of this salt greatly

resemble those of tolylenediamine. The free base has not been isolated.

When solid β-chloro-4-nitroethylbenzene is heated with sodium acetate and glacial acetic acid and the product fractionated under diminished pressure, two substances are obtained, b. p. 189°/16 mm. and 161—163°/16 mm. respectively. The former consists of 4-nitro-β-acetoxyethylbenzene [4-nitrobenzylcarbinyl acetate], and is converted by saponification into 4-*nitro-β-hydroxyethylbenzene* [4-*nitrobenzyl-carbinol*], $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot OH$, b. p. 177°/16 mm. (*benzoyl* derivative is oily; m-*nitrobenzoyl* derivative, m. p. 64—65°; *phenylurethane*, m. p. 127—128°), the constitution of which is proved by its conversion into β-chloro-4-nitroethylbenzene, 66% of which is obtained in the solid form. The fraction of lower b. p., consisting of α-acetoxy-4-nitroethylbenzene, yields the corresponding *alcohol*, b. p. 158°/16 mm. (m-*nitrobenzoyl* derivative, m. p. 152—153°; *phenylurethane*, m. p. 205—206°), which, on oxidation, gives p-nitrobenzoic acid. If the above operations are repeated with liquid β-chloro-4-nitroethylbenzene, the same products result and in the same yields.

β-Chloroethylbenzene, when treated with sodium acetate and acetic anhydride, gives an 85% yield of benzylcarbinyl acetate, b. p. 232°, which, on saponification, regenerates the alcohol. About 15% of α-*acetoxyethylbenzene*, b. p. 222°, is simultaneously produced, which loses some acetic acid on distillation and is saponified to phenylmethylcarbinol, b. p. 204°.

γ-*Acetoxy*-4-*nitropropylbenzene*, b. p. 210—212°/21 mm. (slight decomp.), is obtained as sole product of the action of acetic acid and sodium acetate on γ-chloro-4-nitropropylbenzene.   H. W.

Spectrochemical Notes. I. Hydrated Naphthalenes. II. Spectrochemical Behaviour of Acenaphthene Derivatives. III. Haworth's Dimethyl*cyclo*hexadiene. KARL VON AUWERS (*Ber.*, 1913, 46, 2988—2995).—Δ^1-Dihydronaphthalene and Δ^2-dihydronaphthalene (Straus and Lemmel, this vol., i, 256) have $D_4^{19\cdot2}$ 0·9982, $n_D^{19\cdot1}$ 1·58326, and $D_4^{19\cdot7}$ 0·9928, $n_D^{19\cdot7}$ 1·55489 respectively.

The 1 : 2 : 3 : 4-tetrahydronaphthalene obtained by von Braun and Deutsch (A., 1912, i, 435) is apparently not a homogeneous product, but the specimens obtained by Willstätter and King (this vol., i, 353) and by Straus and Lemmel (*loc. cit.*) agreed together in their properties, namely, $D_4^{17\cdot6}$ 0·9738, $n_D^{17\cdot6}$ 1·54529.

Decahydronaphthalene (Willstätter and King, *loc. cit.*) gave $D_4^{19\cdot1}$ 0·8951, $n_D^{18\cdot0}$ 1·48035.

A comparison of the refractive indices for various wave-lengths indicates that, of the above substances, Δ^1-dihydronaphthalene alone has high exaltation of specific refraction and dispersion; *cyclo*hexadiene is remarkable for showing a slight depression, a phenomenon which has also been observed with *cyclo*hexene. Tetrahydronaphthalene gives results in accord with those expected for a di-substituted benzene derivative, and decahydronaphthalene is approximately normal.

In connexion with the work of Crompton and Smyth (T., 1913, 103, 1302), who come to the decision that acenaphthene and its

mono-halogen derivatives are optically normal, attention is drawn to the fact that their calculations are made with the molecular refraction of naphthalene as a standard. As this substance exhibits a marked exaltation, it follows that the acenaphthene compounds are also optically exalted.

In reference to the two compounds described as dimethyl*cyclo*-hexadienes (Haworth, T., 1913, 103, 1242), one of which has already been prepared (Murawski, *Diss.*, Greifswald, 1911), the author, on optical and also chemical grounds (compare Auwers and Peters, A., 1910, i, 826), regards the substances as being at least mainly composed of the substances $\langle \rangle$:CH$_2$ and $\langle \rangle$:CH$_2$ respectively.

1 : 3-*Dimethyl*cyclo-Δ^1-*hexen*-3-*ol*, which Haworth failed to isolate as the intermediate product in the preparation of the latter of the above two substances, can be obtained from 1-methyl*cyclo*-Δ^1-hexen-3-one by the action of magnesium methyl iodide; it has b. p. 75°/15 mm., $D_4^{16\cdot4}$ 0·9336, $n_D^{17\cdot5}$ 1·47711.   D. F. T.

Organic Radicles. XVIII. Ditertiary Hydrazines. HEINRICH WIELAND and CARL MÜLLER (*Annalen*, 1913, 401, 233—243).—The dissociation of tetra-anisylhydrazine in solution into the free radicles ·N(C$_6$H$_4$·OMe)$_2$ (A., 1912, i, 907) is found to be in harmony with Piccard's colorimetric dilution law (A., 1911, ii, 561).

An interesting contribution to the chemistry of triphenylmethyl is recorded. When heated in boiling *m*-xylene, triphenylmethyl is converted into triphenylmethane and *p*-benzhydryltetraphenylmethane. In boiling *o*-xylene in an atmosphere of carbon dioxide, however, the products are triphenylmethane and a *triphenyl-o-xylylmethane*, CPh$_3$·C$_6$H$_3$Me$_2$, m. p. 165—168°, colourless leaflets. In boiling *p*-xylene, similar results are obtained, triphenylmethane and *triphenyl-p-xylyl-methane*, m. p. 158—159°, long prisms, being formed. These two hydrocarbons do not exhibit halochromy and, like tetraphenylmethane itself, develop intense yellow colorations with concentrated sulphuric acid and a trace of potassium dichromate.

Triphenylmethyl in benzene and triphenylmethyl peroxide in glacial acetic acid are reduced to triphenylmethane by hydrogen and palladium black. Triphenylmethyl and diphenylketen do not react in benzene at 60—70°.   C. S.

Constitution and Colour. III. FRIEDRICH KEHRMANN (*Ber.*, 1913, 46, 3036—3040. Compare A., 1908, i, 699, 993).—The author gives a further explanation of his views on this subject. In the formation of salts from phenazine, phenanthraquinone and similar substances, where the change is accompanied by a marked change in colour, the author is of opinion that the chromophore undergoes modification, for example, by an increase in the valency of one of the elements (nitrogen, oxygen, etc.), or by a change from the ortho- to the para-configuration or vice-versâ.

In reference to the views of Willstätter and Piccard (A., 1908, i, 475), the author draws attention to a constitutive characteristic common

to the coloured salts of the triphenylmethane class and to Wurster's salts; both classes have the auxochrome outside the quinonoid portion of the molecule, so that both may, in a wide sense, be regarded as of meriquinonoid type.　　　D. F. T.

Double Chlorides of Ferric and Ferrous Chloride with Some Aromatic Bases. RAPHAEL MONROE McKENZIE (*Amer. Chem. J.*, 1913, **50**, 308—335).—A number of double chlorides of ferrous and ferric iron with the hydrochlorides of aniline *o*-toluidine, *m*-toluidine, and *p*-toluidine have been prepared by adding the constituent substances together in hydrochloric acid solution, and evaporating over sulphuric acid and solid potassium hydroxide.

The following compounds are described: $FeCl_3,2NH_3PhCl$, crystallising in stout, green needles; $FeCl_3,2NH_3PhCl,H_2O$, crystallising in long, thin, very dark green needles; $FeCl_3,6NH_3PhCl$, crystallising in long, thin, orange-yellow, silky needles; $FeCl_3,6NH_3PhCl,2H_2O$, crystallising in orange needles; $FeCl_3,6NH_3(C_7H_7)Cl,3H_2O[1:2]$, forming brownish-yellow needle clusters; $FeCl_3,2NH_3(C_7H_7)Cl[1:3]$, forming shining yellow plates; $FeCl_3,3NH_3(C_7H_7)Cl[1:3]$: this substance is a viscid, fuming mass which is very deliquescent and could not be crystallised; $FeCl_3,3NH_3(C_7H_7)Cl[1:4]$: forming lustrous, red prisms or plates; $FeCl_2,2NH_3PhCl,2H_2O$, separates from hydrochloric acid in light yellow needles; $FeCl_3,3NH_3(C_7H_7)Cl,6H_2O[1:2]$, crystallising in long, fine, yellow needles, and $FeCl_2,6NH_3(C_7H_7)Cl,HCl,xH_2O[1:2]$: this salt was prepared in the absence of air.　　　J. F. S.

Quaternary Ammonium Salts from Trimethylamine and Arylsulphonyl Chlorides. DANIEL VORLÄNDER and OTTO NOLTE (*Ber.*, 1913, **46**, 3212—3228. Compare Kauffmann and Vorländer, A., 1910, i, 822).—When trimethylamine in aqueous solution is shaken with benzenesulphonyl chloride, a quaternary salt is formed, characterised by forming a sparingly soluble platinichloride which allows of the separation from trimethylammonium platinichloride (compare A., 1910, i, 822). *Benzenesulphonyltrimethylammonium chloride*, $SO_2Ph·NMe_3Cl$, obtained by saturating the platinichloride with hydrogen sulphide, crystallises in long, flat colourless prisms, m. p. 185° (decomp.), which are optically anisotropic. The *platinichloride*, $(PhSO_2·NMe_3)_2PtCl_6$, forms doubly refractive platelets or small, flat prisms, m. p. 215—220° (decomp.). The *aurichloride*, $SO_2Ph·NMe_3·AuCl_4$, yields yellow, doubly refractive needles, m. p. 194—200°. The *picrate* crystallises in splendid, yellow, anisotropic plates and stellate aggregates, m. p. 137°. The *dichromate* is characterised by doubly refractive, orange-yellow crystals, m. p. 202°. The *perchlorate* forms colourless needles, m. p. 145°. The colourless needles of the *stannichloride* have decomp. 245°. The *thallichloride* likewise forms colourless, double refractive needles.

Toluene-p-sulphonyltrimethylammonium platinichloride separates in optically anisotropic platelets and pointed needles. The *dichromate* forms doubly refractive, orange-red plates, decomp. 195°.

Cryptocrystalline α- and β-*naphthalenesulphonyltrimethylammonium platinichlorides* were obtained.

Similar salts were not obtained from triethyl- or tripropyl-amine or from dimethyl- or diethyl-aniline.

The existence of these neutral benzenesulphonylammonium salts stable towards water, which yet contain the very strongly acid benzene-sulphonyl radicle, proves that the salt-forming function of the ammonium does not depend on the positive and negative nature of the radicles.　　　　　　　　　　　　　　　　　E. F. A.

Catalysis on the Basis of Work with Imino-esters. The Problem of Saponification and Esterification. JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1913, **35**, 1774—1779).—A theoretical consideration of the mode of action of acids in accelerating the formation or hydrolysis of esters (compare A., 1908, ii, 29, 167, 472; this vol., ii, 396). Although purely mathematical considerations fail to decide with which oxygen compound (for example, acid or alcohol in esterification) the complex oxonium ion is produced, some decision can be drawn by analogy to the conversion of imino-esters by ammonia or amines into amidines which is also accelerated by acid. In this case the change may occur by interaction of the ammonium ion with the free imino-ester or of the imino-ester cation with free ammonia, according to the alternative schemes : $CPh(:NH)\cdot OMe + H\cdot NH_3^+ \longrightarrow$

$CPh\cdot C(NH_2)(OMe)\cdot NH_3^+ \longrightarrow CPh(:NH)\cdot NH_3^+ + MeOH$

or　$CPh(OMe):NH_2^+ + HNH_2 \longrightarrow CPh(NH_2)(OMe)NH_3^+ \longrightarrow$

$CPh\cdot C(:NH)NH_3^+ + MeOH.$ According to the latter scheme the salts of tertiary amines should be unable to form amidines from imino-esters, and according to Pinner this is actually the case.

The conclusion is therefore to be drawn that in the formation of amidines from imino-esters and amines in the presence of acids, action occurs between the amine (or ammonia) and the ion resulting from the additive compound of the imino-ester with the acid. Extending this analogy to the hydrolysis or formation of esters, it is in these cases most probable that the action is of a hydroxide, water, or alcohol on the oxonium ion of the ester or of the organic acid.　　　D. F. T.

Hydrates of Calcium Oxide and their Molecular Compounds. IV. Compounds of Hydrated Calcium Oxide with Phenols. FEDOR F. SELIVANOV (*J. Russ. Phys. Chem. Soc*, 1913, **45**, 1535—1556. Compare this vol., ii, 214, 406, 407).—The following compounds of calcium hydroxide with phenol have been prepared.

The *diphenolate*, $CaO,H_2O,2PhOH$, apparently analogous to the barium compound obtained by Laurent (*Ann. Chim. Phys.*, 1841, [iii], **3**, 203), is a colourless, hygroscopic compound, and is decomposed by carbon dioxide, although it remains unchanged in a sealed, exhausted tube. It is decomposed by water, with liberation of phenol and calcium hydroxide, a similar action being brought about by ether, benzene, alcohol, etc. On this ground the compound is regarded as possessing the constitution $Ca(OH)_2,2Ph\cdot OH$, which is confirmed by the mode of dissociation of the diphenolate in a vacuum ; the phenol is hence present as phenol of crystallisation, the water possessing a constitutional character. When heated

at 105—110°, the diphenolate is decomposed into phenol, water, and the *monophenoxide*, HO·Ca·OPh, in which the acid properties of the phenol are very faint, so that water effects decomposition into calcium hydroxide and phenol.

The diphenolate forms various hydrates, which may be expressed by the general formula $2Ca(OH)_2,4PhOH,(2n+1)H_2O$, where $n =$ 0, 1, 2, 3 or 4.

The diphenolate is capable of combining with phenol, giving the *tetraphenolate*, $Ca(OH)_2,4PhOH$, and the *hexaphenolate*,

$$Ca(OH)_2,6PhOH.$$

Calcium hydroxide and phenol are also able to form hygroscopic solid solutions, which separate in needles apparently of the rhombic system, and do not dissolve in water, but give with it an oily and an aqueous layer (compare Runge, *Ann. Phys. Chem.*, 1834, **31**, 69; **32**, 308) exhibiting an alkaline reaction. Similar solid solutions are formed by calcium hydroxide and thymol and by magnesium hydroxide and phenol.   T. H. P.

Introduction of Selenium into Organic Compounds. EMIL FROMM and KARL MARTIN (*Annalen*, 1913, **401**, 177—188).—Selenium, unlike sulphur, does not react with stilbene or ethyl cinnamate even by prolonged heating at high temperatures. Contrary to Bauer's statement (this vol., i, 263), 1-phenylbenzoselenazole is obtained in 15—20% yield by vigorously boiling benzanilide and selenium. It is not ruptured by fusion with potassium hydroxide, and forms a *tetrabromide*, $C_{13}H_9NBr_4Se$, m. p. 134°, brick-red powder, and a *tetraiodide*, $C_{13}H_9NI_4Se$, m. p. 84°, greenish-black, metallic crystals, with bromine and with iodine in cold and in boiling chloroform respectively. The four halogen atoms are very easily removed, so the substances probably have the constitution : $C_6H_4\!\!\begin{smallmatrix}>NX_2\\ >SeX_2\end{smallmatrix}\!\!>CPh$.

Equivalent quantities of potassium selenocyanate and *o*-nitrobenzyl chloride in boiling alcohol yield *o-nitrobenzyl selenocyanate*, $C_8H_6O_2N_2Se$, m. p. 77°, decomp. 215°, pale yellow crystals. *o*- and *p*-Chloronitrobenzenes do not react similarly, but 1-chloro-2 : 4-dinitrobenzene rapidly yields 2 : 4-*dinitrophenyl selenocyanate*, m. p. 163°, yellow crystals, which can be crystallised from concentrated nitric acid. 2 : 4-Dinitrophenyl selenocyanate and boiling aqueous alkalis yield a brownish-red solution containing the 2 : 4-dinitrophenylselenol, from which by atmospheric oxidation *di*-2 : 4-*dinitrophenyl diselenide*, $C_{12}H_6O_8N_4Se_2$, m. p. 264—265°, yellow crystals, is precipitated.

Dibenzyl diselenide, like dibenzyl disulphide (this vol., i, 357), reacts additively with bromine and iodine in chloroform to form a *tetrabromide*, $C_{14}H_{14}Br_4Se_2$, m. p. 137°, red powder, and *tetraiodide*, m. p. 98°, dark green, metallic crystals; the additive compounds react with silver oxide or acetate, but are thereby extensively changed, and, unlike the corresponding disulphides (*loc. cit.*), do not yield the diselenoxide.

Seleno-ethers are readily obtained by boiling dibenzyl diselenide with alcoholic sodium ethoxide (2 equiv.) and treating the resulting brownish-red solution of the selenol with an alkyl haloid. Thus

benzyl chloride yields Jackson's dibenzyl selenide, m. p. 45·5°, whilst methyl iodide, ethyl iodide, and ethylene dibromide yield respectively benzyl methyl·selenide, benzyl ethyl selenide, and *dibenzyl ethylene selenide*, $C_2H_4(Se·C_7H_7)_2$, m. p. 68—69°, pale yellow needles. Dibenzyl selenide reacts in chloroform with bromine or iodine to form the *dibromide*, $SeBr_2(C_7H_7)_2$, m. p. 84°, red powder, and *di-iodide*, m. p. 97°, violet crystals, from which, however, the selenoxide cannot be obtained by the action of alkalis, or silver oxide or acetate.

The so-called dibenzyl selenide nitrate obtained by Jackson in 1875 by the action of nitric acid on dibenzyl selenide proves to be *tribenzylselenonium nitrate*, $(C_7H_7)_3Se·NO_3$, decomp. 102—103°; the corresponding *chloride*, $C_{21}H_{21}ClSe$, has m. p. 92°.   C. S.

Nitroquinhydrones. M. M. RICHTER (*Ber.*, 1913, **46**, 3434—3438). —The author has previously pointed out (A., 1911, i, 136) that the introduction of negative groups into the quinone molecule diminishes the basic properties of the oxygen atom, and thus reduces the tendency to quinhydrone formation. In agreement with this view it is found that nitroquinol combines with *p*-benzoquinone to form an unstable quinhydrone, whilst in the case of 2 : 6-dinitroquinol the ability to give rise to quinhydrones has completely disappeared.

Nitroquinhydrone, $C_6H_4O_2,C_6H_3(OH)_2·NO_2$, prepared by evaporating an ethereal solution of *p*-benzoquinone and nitroquinol in the absence of moisture, crystallises in small needles or stout, obliquely cut prisms. It is almost black, and has m. p. 89—90°, with slight previous decomposition at 84°. On exposure to air, it loses *p*-benzoquinone, yielding nitroquinol.

By nitrating the diacetyl derivative of quinol, Hesse (A., 1880, 317) and Nietzki (A., 1883, 465) have obtained a dinitro-derivative, m. p. 96°, which they consider to be the diacetyl derivative of 2 : 6-dinitro-quinol. The author finds, however, that the substance is not a diacetate, but a monoacetyl derivative, one of the acetyl groups being removed during the nitration.

A similar elimination of an acetyl group occurs during the nitration of the diacetyl derivative of toluquinol.

On account of its yellow colour, the monoacetate is considered to be an aci-2 : 6-*dinitro-4-acetoxyphenol* of the annexed constitution. It has m. p. 95·6°, and on treatment with metallic nitrites in aqueous solution yields salts, which decompose explosively when heated. The *sodium* salt forms red needles, containing water (3 mols.), which is lost on exposure to sunlight, the anhydrous salt being orange in colour. The golden-yellow *barium* salt and red *potassium* salt (needles) are also described.

2 : 6-*Dinitro*-1 : 4-*diacetoxybenzene*, $C_6H_2(NO_2)_2(OAc)_2$, prepared by heating the preceding monoacetyl derivative or its sodium and potassium salts with acetic anhydride, crystallises in slender, colourless needles, m. p. 135°.

2 : 6 - *Dinitro* - 1 - *benzoyloxy-4-acetoxybenzene*, $OAc·C_6H_2(NO_2)_2·OBz$, obtained by the action of benzoyl chloride on the monoacetate in
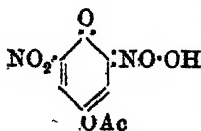
benzene solution in the presence of pyridine, forms small, white needles, m. p. 128—129°.

2 : 6-Dinitroquinol and its monoacetyl derivative possess pronounced acid properties, and combine with aniline, toluidine, benzidine, diphenylformamidine, carbamide hydrazine and pyridine to form coloured additive compounds.

The additive *compound* of aniline with 2 : 6-dinitroquinol crystallises in dark red needles, m. p. 102—103° (decomp.).

The additive *compound* of aniline with *aci*-2 : 6-dinitro-4-acetoxyphenol forms orange needles, m. p. 120° (decomp.).　　　　F. B.

The Constitution of the Monomethyl and Monoethyl Ethers of Aminoresorcinol from the Monomethyl and Monoethyl Ether of Benzeneazo-4-resorcinol. FERDINAND HENRICH and H. BIRKNER (*Ber.*, 1913, **46**, 3380—3384).—The constitution of the ethyl ether obtained by the action of ethyl iodide on the potassium salt of benzeneazo-4-resorcinol has never been finally settled (Will and Pukall, A., 1887, 660). Of the two possible formulæ,

$$\text{NPh:N} \diagdown \begin{array}{c} \text{OH} \\ \diagup \end{array} \text{OEt}$$
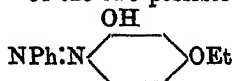
and $\text{NPh:N} \diagdown \begin{array}{c} \text{OEt} \\ \diagup \end{array} \text{OH}$, the former is rendered more probable by the

work of Bechhold (A., 1889, 1155) on the corresponding methyl ether, but the evidence is far from satisfactory.

The reduction products obtained from the nitrosoresorcinol ethers of

the structure $\text{NO} \diagdown \begin{array}{c} \text{OH} \\ \diagup \end{array} \text{OR}$ and $\text{NO} \diagdown \begin{array}{c} \text{OR} \\ \diagup \end{array} \text{OH}$, where R repre-

sents the methyl or ethyl radicle (Henrich and Rhodius, A., 1902, i, 447), will by comparison with the reduction products of the above azo-compounds fix definitely the constitution of the latter. Experiment shows that it is the *o*-amino-ether which is identical with the corresponding ether above, so that the first of the two possible formulæ for the ethyl (and methyl) ether is the correct one, alkylation having occurred in the para-position.

Improved methods are described for the methylation (by methyl sulphate) and ethylation of the benzeneazoresorcinol.　　　D. F. T.

Action of Organomagnesium Derivatives on Trialkylacetophenones. (Mme.) PAULINE RAMART-LUCAS (*Ann. Chim. Phys.*, 1913, [viii], **30**, 349—432).—The reaction between magnesium methyl, ethyl, phenyl, or benzyl haloid and trimethylacetophenone proceeds normally and leads to the formation of the tertiary alcohol,

$$\text{CMe}_3 \cdot \text{CPhR} \cdot \text{OH}.$$
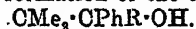
Such carbinols do not exhibit ordinary alcoholic functions, and are readily dehydrated, yielding an unsaturated hydrocarbon. The individual compounds have been described (A., 1910, i, 378 ; 1911, i, 636 ; 1912, i, 351, 449). Magnesium propyl or *iso*propyl iodide acts

as a reducing agent to trimethylacetophenone and converts it into the corresponding secondary alcohol.

a-Phenyl-a-anisyl-ββ-dimethylpropan-a-ol,

$$CMe_3 \cdot CPh(OH) \cdot C_6H_4 \cdot OMe,$$

m. p. 67—68°, b. p. 210—215°/15 mm., and *a-phenyl-a-phenetyl-ββ dimethylpropan-a-ol,* b. p. 215—220°/15 mm., have been prepared from trimethylacetophenone and magnesium anisyl or phenetyl bromide. The following alcohols have been obtained in a similar manner from *aa*-diethylpropiophenone or triethylacetophenone; the yields are generally smaller than those obtained with trimethylacetophenone.
β-Phenyl-γ-methyl-γ-ethylpentan-β-ol, $CMeEt_2 \cdot CPhMe \cdot OH$,   b.   p. 83—84°/3 mm., D_4^{25} 0·9781, n_a 1·51692, n_D 1·52061, $n_β$ 1·52986 ; *aa-diphenyl - β - methyl - β - ethylbutan - a - ol,* $CMeEt_2 \cdot CPh_2 \cdot OH$, b. p. 200—205°/13 mm., D_4^{25} 0·95005, n_a 1·56573, n_D 1·57206 ; by distillation at the ordinary pressure, the latter decomposes into benzophenone and γ-methylpentane.   *aβ-Diphenyl-γ-methyl-γ-ethylpentan-β-ol,*

$$CMeEt_2 \cdot CPh(OH) \cdot CH_2Ph,$$

b. p. 200—202°/15 mm., D_4^{25} 0·9791, n_a 1·55249, n_D 1·55696, $n_β$ 1·57944, yields deoxybenzoin and γ-methylpentane by distillation under atmospheric pressure.   *β-Phenyl-γγ-diethylpentan-β-ol,*

$$CEt_3 \cdot CPhMe \cdot OH,$$

b. p. 160°/18 mm., and *aa-diphenyl-ββ-diethylbutan-a-ol,*

$$CEt_3 \cdot CPh_2 \cdot OH,$$

m. p. 47—48°, b. p. 215—220°/17 mm., are described ; the latter decomposes quantitatively into benzophenone and γ-ethylpentane by distillation at the ordinary pressure.

The preceding tertiary alcohols have been dehydrated by heating them with formic, oxalic, or dilute sulphuric acid, or, best, with a mixture of acetic anhydride and acetyl chloride ; in some cases, the constitutions of the resulting hydrocarbons have been established by the examination of their products of oxidation. Alcohols which contain the group $OH \cdot CPh \cdot OH<$ yield hydrocarbons of the type $\cdot CPh \colon C<$, whilst alcohols which contain the group $>CMe \cdot CPh_2 \cdot OH$ apparently yield a mixture of hydrocarbons of the types $>C \overset{CH_2}{\diagup \diagdown} CPh_2$ and $>CPh \cdot CPh \colon CH_2$; hydrocarbons of the latter type are produced owing to an intramolecular transformation preceding dehydration. β-Phenyl-γγ-dimethyl-Δ^a-butene, $CMe_3 \cdot CPh \colon CH_2$, b. p. 88—92°/15 mm., D_4^{25} 0·8839, n_a 1·49708, n_D 1·50133, $n_β$ 1·51185, $n_γ$ 1·52106, yields acetophenone or trimethylacetophenone by oxidation by chromic and acetic acids or by acidified potassium permanganate respectively. *γ-Phenyl-δδ-dimethyl-$\Delta^β$-pentene,* $CMe_3 \cdot CPh \colon CHMe$, b. p. 91—93°/12 mm., D_4^{25} 0·9064, n_a 1·51100, n_D 1·51550, $n_β$ 1·52710, $n_γ$ 1·53776, yields trimethylacetophenone by oxidation. The dehydration of *aa*-diphenyl-γγ-dimethylpropan-a-ol yields a *substance,* b. p. 159—160°/11 mm., D_4^{25} 1·0031, n_D 1·57589, which is probably a mixture of 1 : 1-diphenyl-2 : 2-dimethyl-*cyclo*propane and 1 : 2-diphenyl-1 : 2-dimethyl*cyclo*propane or βγ-diphenyl-γ-methyl-Δ^a-butene, since it yields both acetophenone and benzophenone by oxidation (A., 1912, i, 449). *aβ-Diphenyl-γγ-dimethyl-Δ^a-butene,* $CMe_2 \cdot CPh \colon CHPh$, b. p. 164—165°/11 mm., yields benzoic
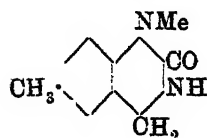
acid, trimethylacetophenone, and a *substance*, $C_{20}H_{20}O$, m. p. 131°, by oxidation. The dehydration of α-phenyl-α-anisyl-ββ-dimethylpropan-α-ol yields a liquid, b. p. 188—189°/15 mm., which is probably a mixture, since its products of oxidation contain *p*-anisic acid and *p*-methoxybenzophenone. Similar remarks apply to the liquid, b. p. 198—200°/15 mm., obtained by the dehydration of α-phenyl-α-phenetyl-ββ-dimethylpropan-α-ol. *αβ - Diphenyl - γ - methyl-γ-ethyl-Δ^α-pentene*, $CMeEt_2 \cdot CPh:CHPh$, b. p. 175—180°/12 mm., D_4^{25} 0·9791, $n_α$ 1·56110, n_D 1·56671, $n_β$ 1·58131, $n_γ$ 1·59467, yields benzoic acid, deoxybenzoin, and αα-diethylpropiophenone by oxidation. *β-Phenyl-γγ-diethyl-Δ^α-pentene*, $CEt_2 \cdot CPh:CH_2$, b. p. 130—132°/15 mm., yields acetophenone and triethylacetophenone by oxidation. αα-Diphenyl-ββ-diethylbutan-α-ol is the only alcohol of the whole series which is not dehydrated by heating with acetic anhydride and acetyl chloride ; the effect of this reagent, like that of boiling, is to decompose the alcohol into benzophenone and γ-ethylpentane.

Further attempts have been made to ascertain the constitution of the acid, $C_{17}H_{18}O_2$, m. p. 173° (*chloride*, $C_{16}H_{17} \cdot COCl$, m. p. 95—96°; *amide*, m. p. 149°), obtained ultimately from diphenyl-ψ-butylcarbinol (A., 1912, i, 623). From its method of formation the acid might be αβ-diphenyl-α-methylbutyric acid, ββ-diphenyl-αα-dimethylpropionic acid, or αα-diphenyl-β-methylbutyric acid ; it is certainly not the first acid (*loc. cit.*). The last acid has been synthesised by the action of sodamide, followed by that of *iso*propyl iodide, on diphenylacetonitrile in boiling benzene ; the resulting αα-*diphenyl-β-methylbutyronitrile*, $CPh_2Pr^β \cdot CN$, b. p. 193—195°/15 mm., is hydrolysed by acetic and hydrochloric acids at 180°, whereby are produced αα-*diphenyl-β-methyl-butyric acid*, $CPh_2Pr^β \cdot CO_2H$, m. p. 166°, its *anhydride*, $C_{34}H_{34}O_3$, m. p. 162—163°, and a *substance*, $C_{16}H_{16}O_2$, m. p. 109—110°. The acid, $C_{17}H_{18}O_2$, m. p. 173°, therefore, is not αα-diphenyl-β-methyl-butyric acid, neither is it ββ-diphenyl-αα-dimethylpropionic acid, m. p. 134—135°, which has been synthesised by Nef. C. S.

Tertiary Derivatives of *o*- and *p*-Aminobenzyl Alcohol. II. JULIUS VON BRAUN, O. KRUBER, and E. AUST (*Ber.*, 1913, **46**, 3056—3069).—It has been previously shown (A., 1912, i, 968) that the group $-CH_2 \cdot OH$ can be introduced into tertiary aromatic amines by the use of an excess of formaldehyde. The present communication deals (1) with the reactivity of the tertiary, basic groups ; (2) the possibility of replacing the hydrogen atoms of the benzene nucleus, and (3) the capacity for condensation of the hydroxyl group present in the side-chain.
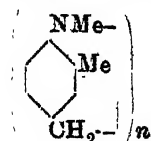
I. Tertiary aminobenzyl alcohols cannot be de-alkylated by means of cyanogen bromide, since the hydroxy-group is also affected. If the latter is protected, however, dealkylation is readily effected. Thus, when 6-dimethylamino-3-methylbenzyl acetate is treated with cyanogen bromide at the ordinary temperature during several days, 6-*cyano-methylamino-3-methylbenzyl acetate*, $CN \cdot NMe \cdot C_6H_3Me \cdot CH_2 \cdot OAc$, b. p. 210°/10 mm., is obtained, whilst, in the same manner, the corresponding *cyano*-compound, b. p. 213—216°/11 mm., is prepared from

4-dimethylamino-3-methylbenzyl acetate. Secondary aminobenzyl alcohols cannot be prepared by saponification of these compounds when the –CH$_2$·OH is in the ortho- or para-position to the cyano-group. When 6-cyanomethylamino-3-methylbenzyl acetate is boiled with aqueous alcoholic sulphuric acid, a *base*, C$_{10}$H$_{12}$ON$_2$, b. p. 166—168°/8 mm., m. p. 59—60°, is obtained (*platinichloride*, m. p. 214°), which is probably a quinoxaline derivative of the annexed formula.
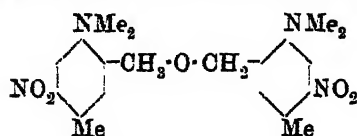
Under similar conditions, the cyano-group of 4-cyanomethylamino-3-methylbenzyl acetate is not replaced; concentrated hydrochloric acid at 120°, however, forms an amorphous *product*, which softens at 70°, and has m. p. 76—80°. It appears to be an anhydro-product of the secondary base (annexed formula), since it combines with dimethylaniline in hot, faintly acid solution to form *trimethyldiaminophenyltolylmethane*, m. p. 55°. That 4-*methylamino-3-methylbenzyl alcohol* is capable of existence in the free state (unlike methyl amino- and ethylamino-benzyl alcohols) is proved by its isolation from the products of the action of a large excess of formaldehyde on monomethyl-*o*-toluidine. It is a yellow oil, b. p. 130—132°/8 mm., which yields a *picrate*, m. p. 112°, and a platinichloride, reddish-yellow crystals, m. p. 173°.

II. 4-*Nitro-6-dimethylamino-3-methylbenzyl alcohol*, b. p. 191—192°/8 mm., m. p. 51° (*platinichloride*, m. p. 198°; *picrate*, m. p. 153°), is formed when a mixture of nitric and sulphuric acids is slowly added to a solution of 6-dimethylamino-3-methylbenzyl alcohol in concentrated sulphuric acid, the temperature being kept at 0° during two hours and the mixture subsequently being allowed to remain for three hours at the ordinary temperature. Should the temperature be allowed to rise, considerable quantities of a substance are formed which can be isolated in the form of its sparingly soluble *sulphate.* The free *base* (annexed formula) has m. p. 136°, and is not hydrolysed by prolonged warming with 2N-sulphuric acid. The *picrate* has m. p. 154°. 6-*Nitro-4 dimethylamino-3-methylbenzyl alcohol*, b. p. 204—208°/11 mm. (slight decomp.), m. p. 64—65° (*platinichloride*, reddish-yellow, crystalline powder), is similarly prepared from 4-dimethylamino-5-methylbenzyl alcohol.
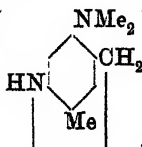
4-Nitro-6-dimethylamino-3-methylbenzyl alcohol is readily reduced by stannous chloride and hydrochloric acid to 4-*amino-6-dimethylamino-3-methylbenzyl alcohol*, white crystals, m. p. 103—104°. The base is completely decomposed by distillation, yields a *picrate*, m. p. 179°, a viscous *acetyl* compound, and a *monobenzoyl* compound, m. p. 135°. It is slowly diazotised by nitrous acid. It combines with allylthiocarbimide, yielding the crystalline *compound*, NMe$_2$·C$_6$H$_2$Me(CH$_2$·OH)·NH·CS·NH·C$_3$H$_5$, m. p. 178°, and with salicylaldehyde, yielding the *salicylidene* compound, m. p. 70°,

Although the composition of the base seems, therefore, to be firmly

established, certain indications lead the authors to consider that there is some tendency for it to pass into the *anhydro*-compound (annexed formula) in the presence of aqueous mineral acids; thus the base, in itself colourless, dissolves in aqueous acid with a reddish-yellow coloration, whilst the colourless *hydrochloride* becomes yellow on exposure to moist air; further, the base, like the readily dehydrated p-aminobenzyl alcohol and its monoalkyl derivatives and unlike the tertiary amino-alcohols in which dehydration is impossible, readily condenses with aromatic compounds in faintly acid solution to form derivatives of diphenylmethane. So with dimethylaniline, it yields *4-amino-2 : 4′-tetramethyldiamino-3-methyldiphenylmethane*, m. p. 92° (*benzoyl* derivative, m. p. 134°), whilst the corresponding *compound* from aniline is oily and gives a *diacetyl* derivative, m. p. 207°.

III. The condensation of dimethylaminobenzyl alcohol and its homologues with dimethylaniline and its homologues, which does not occur to an appreciable extent with aqueous acid solution, can be effected at higher temperatures by the help of zinc chloride. The authors have already shown that a derivative of diphenylmethane is thus formed in the case of 4-dimethylaminobenzyl alcohol and dimethylaniline (A., 1912, i, 970), and now show by a series of examples that the reaction takes a similar course with their homologues containing methyl groups. Thus 4-dimethylaminobenzyl alcohol and dimethyl-m-toluidine yield *4 : 4′-tetramethyldiaminophenyl-o-tolylmethane*, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3Me \cdot NMe_2$, b. p. 240—244°/8 mm. (*platinichloride*, m. p. 188—190° after darkening from 150°; *picrate*, m. p. about 70°), the constitution of which follows from its identity with the product obtained by the action of dimethyl-m-toluidine on 4-dimethylaminobenzyltoluidine in hydrochloric acid solution (compare Cohn and Fischer, A., 1900, i, 690).

Trimethyldiaminophenyl-m-tolylmethane (see above) is difficultly converted by exhaustive methylation into a pure di-quaternary iodide. When heated at 120° during three hours with methyl iodide and methyl alcohol, it yields a mono-*methiodide*, $C_{19}H_{27}N_2I$, m. p. 152°, which, when distilled in a vacuum, gives 4 : 4′-tetramethyldiaminophenyl-m-tolylmethane (obtained from 4-dimethylamino-3-methylbenzyl alcohol and dimethylaniline, A., 1912, i, 970), which is further identified by means of its picrate, m. p. 183°.

The statement of the D.R.-P. No. 107712, that aminobenzylaniline and its homologues only condense with amines which do not contain a substituent in the para-position is incorrect, at any rate as far as p-toluidine is concerned; when dimethylaminobenzyltoluidine is treated with p-toluidine in hydrochloric acid solution, 2′-*amino-4-dimethylaminophenyl-m-tolylmethane*, $NH_2 \cdot C_6H_3Me \cdot CH_2 \cdot C_6H_4 \cdot NMe_2$, b. p. 240—245°/10 mm., m. p. 87°, is obtained in poor yield. The *picrate* has m. p. 180—181°. When heated with methyl iodide and methyl alcohol, the base yields a di-quaternary iodide, m. p. 204° (previously obtained from 2-dimethylamino-5-methylbenzyl alcohol and dimethyl-

aniline), which, when heated in a vacuum, yields 4 : 6'-tetramethyl-diaminophenyl-*m*-tolylmethane, m. p. 84°.

4-Dimethylamino-3-methylbenzyl alcohol condenses with dimethyl-*o*-toluidine to form *s-tetramethyldiaminodi*-m-*tolylmethane*,

$$CH_2(C_6H_3Me \cdot NMe_2)_2.$$
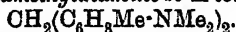
yellow oil, b. p. 228—229°/11 mm.; *picrate*, m. p. 187°; *platinichloride*, needles, m. p. 224° after darkening at 222°; *methiodide*, m. p. 199° after softening at about 190°. The constitution of the base is proved by its identity with the product obtained by the methylation of *s*-dimethyldiaminodi-*m*-tolylmethane prepared by Gnehm and Blumer by the condensation of formaldehyde with methyl-*o*-toluidine.

The liquid nature of many of the basic derivatives of diphenyl-methane and the frequently indistinct melting point of their salts has led the authors to investigate the suitability of their nitro-derivatives in characterising them. They seem to be generally well adapted for this purpose. According to the quantity of nitric acid used, mono- or di-nitro-derivatives can be obtained which are crystalline, and can readily be reduced by stannous chloride to the corresponding mono- and di-amino-compounds. In this connexion, the following substances have been prepared : 2 : 2'-*dinitro*-4 : 4'-*tetramethyldiaminodi*-m-*tolyl-methane*, $CH_2[C_6H_2Me(NO_2) \cdot NMe_2]_2$, yellow leaflets, m. p. 125°; 4 : 4'-dinitro-2 : 2'-tetramethyldiaminodi-*m*-tolylmethane, m. p. 102°, which, on reduction, yields the corresponding *di-amino*-compound ; 2' : 4-*dinitro*-2 : 4'-*tetramethyldiaminophenyl*-m-*tolylm*-*thane*,

$$NMe_2 \cdot C_6H_2Me(NO_2) \cdot CH_2 \cdot C_6H_3(NO_2) \cdot NMe_2,$$
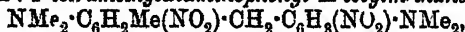
dark red crystals, m. p. 187°, which is reduced to the *diamino*-derivative, colourless crystals, m. p. 140°; 2'-*nitro*-2 : 4'-*tetramethyl-diaminophenyl*-m-*tolylmethane*, $NMe_2 \cdot C_6H_3Me \cdot CH_2 \cdot C_6H_3(NO_2) \cdot NMe_2$, red crystals, m. p. 94°; corresponding *amino*-compound, m. p. 97—98°.

According to Biehringer (A., 1897, i, 73), 2 : 2'-diamino-4 : 4'-tetra-methyldiaminodiphenylmethane loses ammonia when heated with hydrochloric acid with formation of an acridine ring. The authors find that a similar ring formation does not occur when the hydrogen atoms of the amino-group are replaced by methyl. When heated with hydrochloric acid at a temperature not exceeding 180°, the bases are unchanged ; under more drastic treatment, formaldehyde is eliminated, but the liberation of methyl-, dimethyl- or trimethyl-amine could not be detected.   H. W.

Tertiary Derivatives of *o*- and *p*-Aminobenzyl Alcohol. III. JULIUS VON BRAUN and OTTO KRUBER (*Ber.*, 1913, **46**, 3460—3470).—In previous papers (A., 1912, i, 968; preceding abstract), the authors have shown that tertiary aromatic amines of the dialkylaniline type readily condense with formaldehyde, either alone or in the presence of hydrochloric acid, yielding derivatives of 2 : 2'- and 4 : 4'-tetra-alkyl-diaminodiphenylmethane, $CH_2(C_6H_4 \cdot NMe_2)_2$, and of *o*- and *p*-dialkyl-aminobenzyl alcohols. The reaction has now been extended to the following amines in order to ascertain the effect of nuclear substituents on the course of the condensation : (1) dimethyl-*m*-toluidine, (2) diethyl-*m*-toluidine, (3) dimethyl-*m*-chloroaniline, (4) phenylbenzyl-methylamine, (5) dimethylcumidine, (6) dimethyl-*p*-chloroaniline,

(7) dimethyl-*p*-bromoaniline, (8) dimethyl-*p*-bromo-*m*-toluidine, and (9) dimethyl-*o*-chloroaniline.

The meta-substituted amines, (1) and (3), resemble the unsubstituted dimethylaniline in that they are almost quantitatively converted by the theoretical amount of formaldehyde ($\frac{1}{2}$ mol.) into the corresponding diphenylmethane derivatives, whilst, with excess of formaldehyde, only small yields of the dialkylaminobenzyl alcohols are obtained. The behaviour of the para-substituted amines (5)—(8) is similar to that of dimethyl-*p*-toluidine. They do not form diphenylmethane derivatives, but, with excess of the aldehyde, give rise to the dialkylaminobenzyl alcohols in good yield.

In the case of the amines 6, 7 and 8, containing a halogen atom in the para-position to the dimethylamino-group, the prolonged action of formaldehyde in the presence of hydrochloric acid causes partial oxidation of the alcohol to the corresponding acid.

It is also found that dimethyl-*o*-chloroaniline condenses with formaldehyde much more readily than dimethyl-*o*-toluidine, and the conclusion is, therefore, drawn that the inhibiting effect of ortho-substituents on the reactivity of the para-hydrogen atoms of the dialkylanilines is not always the same (compare Friedländer, A., 1899, i, 350), but may vary considerably with the nature of the substituent.

Dimethyl-*m*-toluidine condenses with formaldehyde ($\frac{1}{2}$ mol.), yielding 4 : 4'-tetramethyldiaminodi-*o*-tolylmethane, b. p. 253—256°/12 mm., m. p. 82° (*picrate*, m. p. 150°); with excess of formaldehyde it yields *4-dimethylamino-3-methylbenzyl alcohol* as a yellow, almost odourless oil, b. p. 138—142°/10 mm., which forms a *picrate*, felted needles, m. p. 145—146°, an oily *methiodide*, a *platinichloride*, needles, m. p. 178°, and *m-nitrobenzoyl* derivative, m. p. 64°.

4 : 4'-*Tetraethyldiaminodi-o-tolylmethane*, $CH_2(C_6H_3Me\cdot NEt_2)_2$, b. p. 260—266°/10 mm., m. p. 54—55°, and *4-diethylamino-3-methylbenzyl alcohol*, b. p. 160—170°/18 mm. (decomp.) are formed by condensing diethyl-*m*-toluidine with formaldehyde. The alcohol is very resistant towards reducing agents and forms a *picrate*, m. p. 100—103°; the *platinichloride* and *methiodide* are oils.

m-Chlorodimethylaniline condenses with formaldehyde ($\frac{1}{2}$ mol.) in the presence of hydrochloric acid, yielding 4 : 4'-*tetramethyldiaminodi-o-chlorodiphenylmethane*, b. p. 272—276°/9 mm., m. p. 96—97° [*picrate*, m. p. 130—133°; *platinichloride* (decomp. 230°)], which on oxidation with lead dioxide is converted into 4 : 4'-*tetramethyldiamino*-2 : 2'-*dichlorobenzhydrol*. This forms colourless crystals, m. p. 121°, yields blue solutions in glacial acetic acid, and condenses with dimethylaniline in acid solution to form 4 : 4' : 4''-*hexamethyltriamino*-2 : 2'-*dichlorotriphenylmethane*, $NMe_2\cdot C_6H_4\cdot OH(C_6H_3Cl\cdot NMe_2)_2$, which separates from alcohol in lustrous crystals, m. p. 193°, and is oxidised to a blue *dye* of extraordinary fastness to light.

2-Chloro-4-dimethylaminobenzyl alcohol, obtained in poor yield (2%) from *m*-chlorodimethylaniline and excess of formaldehyde, forms a yellow oil, b. p. 156—160°/9 mm.; the *picrate* has m. p. 150°, the *platinichloride*, m. p. 184°.

p-Benzylmethylaminobenzyl alcohol, $C_7H_7\cdot NMe\cdot C_6H_4\cdot CH_2\cdot OH$, prepared from benzylmethylaniline, distils with decomposition at 230°

under diminished pressure, and, therefore, could not be isolated in a pure condition.

Dimethylcumidine gives rise to 6-*dimethylamino*-3-*isopropylbenzyl alcohol*, a yellow oil, b. p. 140—144°/8 mm. (*picrate*, m. p. 118—119°; *methiodide*, m. p. 147°; *platinichloride*, reddish-yellow leaflets, m. p. 187°), which condenses with 1-phenylpiperidine in the presence of zinc chloride, yielding 4-*piperidino*-6'-*dimethylamino*-3'-*isopropyldiphenylmethane*, NMe₂·C₆H₃Prᵝ·CH₂·C₆H₄·NC₅H₁₀, as a viscid oil, b. p. 260—266°/9 mm. (*picrate*, m. p. 100—105°; *platinichloride*, m. p. 219—220°).

Dimethyl-*p*-chloroaniline very readily condenses with formaldehyde, yielding 5-*chloro*-2-*dimethylaminobenzoic acid* (*hydrochloride*, m. p. 172—173°; *platinichloride*, m. p. 190°) and 5-*chloro*-2-*dimethylaminobenzyl alcohol*, a yellow oil, b. p. 158—160°/10 mm. (*picrate*, m. p. 152°; *methiodide*, m. p. 137°), which condenses with *p*-chlorodimethylaniline and dimethylaniline, yielding 5 : 5'-*dichloro*-2 : 2'-*tetramethyldiaminodiphenylmethane*, CH₂(C₆H₃Cl·NMe₂)₂, b. p. 240—260°/14 mm., m. p. 151°, and 5-*chloro*-2 : 4'-*tetramethyldiaminodiphenylmethane*, b. p. 242—246°/12 mm., m. p. 144° (*picrate*, yellow leaflets, m. p. 165°; *methiodide*, m. p. 195°), respectively.

The behaviour of dimethyl-*p*-bromoaniline is similar, 5-*bromo*-2-*dimethylaminobenzoic acid* (not isolated) and 5-*bromo*-2-*dimethylaminobenzyl alcohol*, b. p. 160—170°/13 mm. (*picrate*, m. p. 153°) being produced.

By brominating dimethyl-*m*-toluidine, Wurster and Riedel⁻ (A., 1880, 109) obtained a bromo-compound of m. p. 98°, b. p. 276°. The authors find, however, that the bromination of pure dimethyl-*m*-toluidine in glacial acetic acid solution yields a bromo-derivative, m. p. 55°, b. p. 146—148°/17 mm., which decomposes completely on distillation under ordinary pressure. It forms a methiodide, m. p. 177°, identical with that described by Fischer and Windaus (A., 1900, i, 484), and accordingly must be a p-*bromodimethyl*-m-*toluidine*.

5-*Bromo*-2-*dimethylamino*-4-*methylbenzyl alcohol*, obtained together with the corresponding *acid* by the condensation of the preceding bromodimethyltoluidine with formaldehyde, has b. p. 168—172°/14 mm., forms a *picrate*, crystallising in leaflets, m. p. 150°, and on nitration in concentrated sulphuric acid solution yields a yellow, crystalline *nitro*-derivative, m. p. 83°, of the annexed constitution.

Me
Br
NO₂   NMe₂
CH₂·OH
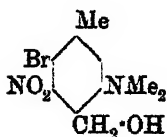
3 - *Chloro* - 4 - *dimethylaminobenzyl alcohol*, b. p. 168—170°/11 mm. (*picrate*, m. p. 130°; *platinichloride*, m. p. 168°; *methiodide*, m. p. 119°; *nitro*-derivative, C₉H₁₁O₃N₂Cl, m. p. 80°), prepared from *o*-chlorodimethylaniline and excess of formaldehyde in the presence of hydrochloric acid, condenses with dimethylaniline and *o*-chlorodimethylaniline to form3-*chloro*-4 : 4'-*tetramethyldiaminodiphenylmethane*, NMe₂·C₆H₃Cl·CH₂·C₆H₄·NMe₂, a liquid, b. p. 248—250°/12 mm. (*picrate*, m. p. 166—167°; *dimethiodide*, m. p. 201°), and 3 : 3'-*dichloro*-4 : 4'-*tetramethyldiaminodiphenylmethane*, CH₂(C₆H₃Cl·NMe₂)₂, which forms a viscid oil, b. p.

258—260°/10 mm., yields a deep yellow *dinitro*-derivative, m. p. 144°, and is also obtained by the direct condensation of *o*-chlorodimethyl-aniline with the calculated amount of formaldehyde.　F. B.
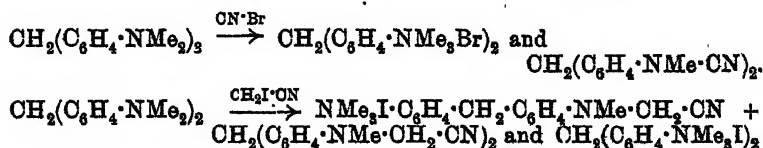
Steric Hindrance with Tertiary Aromatic Amines. JULIUS VON BRAUN and OTTO KRUBER (*Ber.*, 1913, **46**, 3470—3479).—In preparing the methiodides of the tetramethyldiaminodiarylmethanes, tabulated below, the authors found that the bases 5, 7, and 8, containing a substituent in the ortho-position to one of the dimethylamino-groups, combined rapidly with two molecules of methyl iodide, whilst in the case of the amines 2, 4, and 9, in which substituents occur in the ortho-position to both the dimethylamino-groups, the addition of methyl iodide proceeded very slowly. It would thus appear that the occurrence of the reaction at the sterically unhindered dimethylamino-group induces the same reaction at the sterically hindered group.

(1) 4 : 4'-Tetramethyldiaminodiphenylmethane.
(2) 4 : 4'-Tetramethyldiaminodi-*m*-tolylmethane.
(3) 4 : 4'-Tetramethyldiaminodi-*o*-tolylmethane.
(4) 6 : 6'-Tetramethyldiaminodi-*m*-tolylmethane.
(5) 4 : 4'-Tetramethyldiaminophenyl-*m*-tolylmethane.
(6) 4 : 4'-Tetramethyldiaminophenyl-*o*-tolylmethane.
(7) 4 : 6'-Tetramethyldiaminophenyl-*m*-tolylmethane.
(8) 4 : 4'-Tetramethyldiamino-*o* : *m*-ditolylmethane.
(9) 6 : 4'-Tetramethyldiaminodi-*m*-tolylmethane.
(10) 4 : 6'-Tetramethyldiamino-*o* : *m*-ditolylmethane.

The addition of methyl iodide to tertiary aromatic amines is, however, not particularly subject to steric influences, and the authors have, therefore, examined the behaviour of the above amines towards cyanogen bromide and iodoacetonitrile.

With respect to the action of cyanogen bromide on tertiary aromatic amines, it has already been shown that whilst sterically unhindered amines react with extreme ease at the ordinary temperature yielding compounds of the type $R \cdot NMe_3Br$ and $R \cdot NMe \cdot CN$, amines containing an ortho-substituent enter into reaction with great difficulty. In the case of iodoacetonitrile, the presence of an ortho-substituent completely suppresses the reaction.

In agreement with the results obtained by the addition of methyl iodide, it was found that the di-*o*-substituted amines 2, 4, and 9 do not react with either cyanogen bromide or iodoacetonitrile, whilst the amines 5, 7, 8, and 10, containing a substituent in the ortho-position to only one of the dimethylamino-groups, enter into reaction as readily as the amines 1, 3, 6 in which steric influences are completely absent, the reactions proceeding according to the following scheme:

$$CH_2(C_6H_4 \cdot NMe_2)_2 \xrightarrow{CN \cdot Br} CH_2(C_6H_4 \cdot NMe_3Br)_2 \text{ and}$$
$$CH_2(C_6H_4 \cdot NMe \cdot CN)_2.$$

$$CH_2(C_6H_4 \cdot NMe_2)_2 \xrightarrow{CH_2I \cdot CN} NMe_3I \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot NMe \cdot CH_2 \cdot CN +$$
$$CH_2(C_6H_4 \cdot NMe \cdot CH_2 \cdot CN)_2 \text{ and } CH_2(C_6H_4 \cdot NMe_3I)_2$$

That the presence of meta-substituents has little effect on the inter-

action of tertiary amines and cyanogen bromide or iodoacetonitrile has been shown by the behaviour of *m*-chlorodimethylaniline and dimethyl-*m*-toluidine, both of which react with these compounds almost as readily as dimethylaniline and dimethyl-*p*-toluidine.

m-*Tolyltrimethylammonium bromide*, obtained together with m-*tolyl-methylcyanamide*, $C_6H_4Me\cdot NMe\cdot CN$, a yellow oil, b. p. 142—144°/8 mm., by the action of cyanogen bromide on dimethyl-*m*-toluidine, volatilises at about 200° without melting.

m-Chlorodimethylaniline and cyanogen bromide give rise to m-*chlorophenylmethylcyanamide*, $C_6H_4Cl\cdot NMe\cdot CN$. This has m. p. 72°, and is readily hydrolysed to *m*-chloromethylaniline, which is thus obtained more readily and in better yield than by the direct methylation of *m*-chloroaniline, Iodoacetonitrile reacts with dimethyl-*m*-toluidine, yielding m-*tolyltrimethylammonium iodide*, m. p. 177°, and *methylcyanomethyl*-m-*toluidine* [N-*methyl*-m-*toluidinoacetonitrile*],
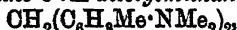
$$C_6H_4Me\cdot NMe\cdot CH_2\cdot CN,$$
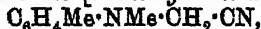
a yellow oil, b. p. 158°/8 mm. With *m*-chlorodimethylaniline it yields m-*chlorophenyltrimethylammonium iodide*, m. p. 187°, and *methylcyanomethyl*·m-*chloroaniline* [N-*methyl*-m-*chloroanilinoacetonitrile*],

$$C_6H_4Cl\cdot NMe\cdot CH_2\cdot CN,$$
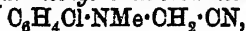
b. p. 175—180°/9 mm.

4 : 4'-*Tetramethyldiamino*-o : m-*ditolylmethane*,

$$CH_2(C_6H_3Me\cdot NMe_2)_2,$$

prepared by condensing 4-dimethylamino-3-methylbenzyl alcohol with dimethyl-*m*-toluidine in the presence of zinc chloride, is a yellow oil, b. p. 244—246°/10 mm., and readily combines with methyl iodide to form a *dimethiodide*, m. p. 232—234°.

6 : 4'-*Tetramethyldiaminodi*-m-*tolylmethane*, obtained from 2-dimethylamino-5-methylbenzyl alcohol and dimethyl-*o*-toluidine in a similar manner, has b. p. 218—222°/11 mm., yields a *picrate*, m. p. 95°, and forms a *dimethiodide*, lustrous leaflets, m. p. 195°.

4 : 6'-*Tetramethyldiamino*-o : m-*ditolylmethane*, prepared from 2-dimethylamino-5-methylbenzyl alcohol and dimethyl-*m*-toluidine, has b. p. 230—235°/12 mm., and forms a *dimethiodide*, m. p. 209°.
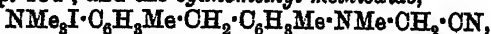
Of the compounds produced by the action of cyanogen bromide and iodoacetonitrile on the 10 amines enumerated above, the following are described : the *dicyano*-compound,

$$CH_2(C_6H_3Me\cdot NMe\cdot CN)_2$$
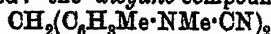
(lustrous leaflets, m. p. 130°), derived from 6, together with the corresponding *dicyanomethyl* compound,

$$CH_2(C_6H_3Me\cdot NMe\cdot CH_2\cdot CN)_2,$$
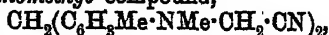
needles, m. p. 134°, and the *cyanomethyl-methiodide*,

$$NMe_3I\cdot C_6H_3Me\cdot CH_2\cdot C_6H_3Me\cdot NMe\cdot CH_2\cdot CN,$$

lustrous leaflets, m. p. 143°; the *dimethiodide* from 6 has m. p. 243°. The *dicyano*-compound from 3 has m. p. 125°; the *dimethiodide*, m. p. 205°.

The *dicyano*-derivative from 7 forms long needles, m. p. 151°; the *dicyanomethyl* derivative, leaflets, m. p. 104°; the corresponding *cyanomethyl-methiodide*,

Me

NMe₃I⟨ ⟩·CH₂⟨ ⟩   or   CN·CH₂·NMe⟨ ⟩·CH₂⟨ ⟩ ,

NMe·CH₂·CN   NMe₂I
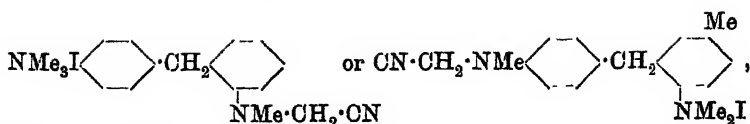
has m. p. 165°.

Of the derivatives formed by the action of iodoacetonitrile on the amines 5, 8 and 10, only the *dimethiodides* and the *dicyanomethyl* compound derived from 8 were isolated.

The action of cyanogen bromide on 5, 8 and 10 yields the corresponding *dicyano*-derivatives, which have m. p. 96—97°, 90—91°, and 120° (with previous softening at 115°) respectively.

The behaviour of 4 : 4'-tetramethyldiamino-3-chlorodiphenylmethane and 2 : 4'-tetramethyldiamino-5-chlorodiphenylmethane towards cyanogen bromide and iodoacetonitrile is similar to that of the analogously constituted methyl compounds 5 and 7. The first-named base yields a *dicyano*-derivative, m. p. 157°; the corresponding *dicyanomethyl* compound and *cyanomethyl-methiodide* have m. p. 105° and 141°.   F. B.

Oxonium Compounds. III. GEORGE L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*,1913, **45**, 1391—1414. Compare A., 1912, i, 971).— The greater part of this paper has been already abstracted (this vol., i, 1183).

The author further shows experimentally that, in the action of 3 mols. of diphenylmethyl ethyl ether on magnesium propyl iodide under the conditions employed by Tschelincev and Pavlov (this vol., i, 461), part of the etherate passes into solution. During distillation, this etherate is subjected to a very high temperature (280°), and it is hence not surprising that it decomposes with formation of tetraphenylethane. Other results obtained by these authors are also criticised.

Gorski's results (this vol.. i, 462) are not new (see Oddo, A., 1911, i, 443).   T. H. P.

Triphenylthiocarbinol. DANIEL VORLÄNDER and ERNST MITTAG (*Ber.*, 1913, **46**, 3450—3460).—Although triphenylcarbinol contains three phenyl groups its acid properties are no greater than those of an aliphatic alcohol. It has, however, more pronounced basic properties than any other tertiary alcohol, and shows a marked tendency to lose its hydroxyl group.

This behaviour is in accordance with the rules laid down by Vorländer (A., 1902, i, 309), according to which the reactivating influence of unsaturated groups on adjacent atoms or groups attains a maximum in the 3 : 4-position. The unsaturated phenyl groups in triphenylcarbinol occupy the 3 : 4-position with respect to the oxygen atom, which, therefore, is very mobile and readily separates from the molecule in the form of hydroxyl: (O⁴=C³)·C²·O¹·H. In order to ascertain the effect of substituting sulphur in place of oxygen in the above system, the authors have examined the behaviour of triphenylcarbinyl-

4 *u* 2

mercaptan, and find that, in accordance with the above rule, it shows a marked tendency to rupture between the sulphur and central carbon atoms. Its acid properties are scarcely more pronounced than those of hydrogen sulphide or methyl mercaptan. It dissolves in alkali hydroxides, but the salts thus formed are readily hydrolysed by water. It comparison with other thio-alcohols it shows a marked tendency to lose the thiol group. On treatment with concentrated sulphuric acid or perchloric acid it evolves hydrogen sulphide and is transformed into triphenylcarbinol. A similar decomposition occurs when the thiocarbinol is heated with acetic acid or acetic anhydride. With hydrogen chloride in benzene solution it yields hydrogen sulphide and ω-chlorotriphenylmethane. When boiled with dilute aqueous alkali hydroxides it slowly forms the corresponding alkali sulphides.

The behaviour towards silver salts is very characteristic. It instantly reacts with silver nitrate in alcoholic solution, yielding silver sulphide and triphenylcarbinol; in this respect it resembles the hydrosulphides of the alkali-metals or metals of the alkaline earths. With silver perchlorate in benzene solution it forms silver sulphide and triphenylmethyl perchlorate.

The benzoyl and acetyl derivatives, and also the methyl ether, resemble the parent substance in being readily ruptured between the sulphur and central carbon atoms. Thus, the methyl ether on treatment with alcoholic silver nitrate yields the silver salt of methyl mercaptan, whilst with concentrated sulphuric acid or dilute hydrochloric acid, the mercaptan itself is produced; with alcoholic silver nitrate the benzoyl derivative yields silver thiobenzoate.

The readiness with which triphenylcarbinylmercaptan suffers rupture between the sulphur and central carbon atoms indicates that the union between these atoms is very similar to that between the chlorine and carbon atoms in ω-chlorotriphenylmethane. On the other hand, the union between the cyano-group and central carbon atom in triphenylacetonitrile is much more stable, for this compound does not react with silver nitrate, and is unattacked by sulphuric or perchloric acids.

Attempts to prepare triphenylcarbinyl mercaptan and triphenylacetonitrile by the action of hydrogen sulphide and hydrogen cyanide on triphenylcarbinol were unsuccessful.

By passing hydrogen sulphide into ω-chlorotriphenylmethane at 120—150°, triphenylmethane, sulphur, and hydrogen chloride were produced.

Reduction of the thiocarbinol with sodium and alcohol yields triphenylmethane and sodium sulphide, whilst the action of chlorine in carbon tetrachloride solution gives rise to ω-chlorotriphenylmethane.

The behaviour of triphenylmethyl disulphide, $(CPh_3)_2S_2$, has also been investigated. On treatment with perchloric acid it liberates hydrogen sulphide, but not so readily as the thiocarbinol. It is transformed by chlorine into ω-chlorotriphenylmethane.

Triphenylcarbinyl mercaptan [ω-*thioltriphenylmethane*], $CPh_3 \cdot SH$, prepared by saturating a solution of sodium ethoxide in ethyl alcohol with hydrogen sulphide and heating the resulting solution of sodium

hydrosulphide with ω-chlorotriphenylmethane, separates from alcohol in long, white, prismatic crystals, m. p. 107°. The *sodium* salt is obtained by shaking an ethereal solution of the thiocarbinol with concentrated aqueous potassium hydroxide. The *lead* and *mercuric* salts are also described.

The acetyl and benzoyl derivatives, prepared by the action of the acid chlorides on the carbinol in pyridine solution, have m. p. 139—141° and 185° respectively, and are decomposed by sulphuric acid with the evolution of hydrogen sulphide (compare Wheeler, - A., 1902, i, 28; Meyer and Fischer, 1911, i, 120).

Triphenylmethyl disulphide is obtained in colourless needles by the addition of sulphuryl, chloride to an ice-cold, alcoholic solution of the sodium salt of the thiocarbinol; it becomes yellow, and begins to decompose at 140°, m. p. about 155°.

Triphenylmethyl methyl sulphide, prepared by the action of methyl sulphate on a solution of the thiocarbinol in methyl-alcoholic sodium methoxide, or by heating the carbinol with methyl iodide and potassium hydroxide in methyl-alcoholic solution, has m. p. 105—106° (compare Meyer and Fischer, *loc. cit.*). F. B.

Action of Dimethylamine on the Iodohydrins of Styrene; Study of the Two Phenyldimethylaminoethanols. MARC TIFFENEAU and ERNEST FOURNEAU (*Bull. Soc. chim.*, 1913, [iv], 13, 971—981).—The authors have confirmed Krassusky's views that the formation of an amino-alcohol from a chloro- or iodo-hydrin takes place through the intermediate formation of an ethylene oxide (compare A., 1908, i, 139). The two isomeric styrene iodohydrins, $OH \cdot CHPh \cdot CH_2I$ and $CHPhI \cdot CH_2 \cdot OH$, both react with dimethylamine to give the same β-dimethylamino-α-phenylethanol, $OH \cdot CHPh \cdot CH_2 \cdot NMe_2$, which is also obtained by the interaction of styrene oxide and dimethylamine. It is a liquid, b. p. 132—133°/15 mm., D_4^0 1·021 (compare Tiffeneau, *Ann. Chim. Phys.*, 1907, [viii], 10, 342). It yields a *hydrochloride*, m. p. 147°; a *picrate*, m. p. 35—40°; a benzoyl hydrochloride, m. p. 210° (compare *loc. cit.*); a *morpholone hydrochloride*, m. p. 229°, from interaction in benzene solution with ethyl chloroacetate; a *methiodide*, m. p. 225°; a *methochloride*, m. p. 199—200°, by the action of silver chloride on the methiodide. This methochloride, which is the hydrochloride of secondary phenylcholine, gives an *aurichloride*, m. p. 154°, soluble in water, and a *picrate*, prismatic needles, m. p. 195°.

Styrene methyliodohydrin reacts similarly with dimethylamine, yielding β-*dimethylamino-α-methoxy-α-phenylethane*, $OMe \cdot CHPh \cdot CH_2 \cdot NMe_2$, b. p. 105—107°/15 mm., 229—230°/760 mm.; D_4^0 1·0013, which gives a *hydrochloride*, m. p. 228°; a *hydriodide*, m. p. 205°, and a *methiodide*, m. p. 180°. Styrene ethyliodohydrin similarly yields β-*dimethyl-amino-α-ethoxy-α-phenylethane*, b. p. 118—119°/19 mm., 229—230°/760 mm., D_4^0 0·9623, giving a *hydrochloride*, m. p. 134°, a *hydriodide*, m. p. 153°, and a *methiodide*, m. p. 157°.

In further proof that the styrene iodohydrin, $CHPhI \cdot CH_2 \cdot OH$, does not yield the corresponding dimethylaminoethanol,

$$NMe_2 \cdot CHPh \cdot CH_2 \cdot OH,$$

but the isomeric ethanol, the former has been prepared by other methods and characterised as follows :

Phenylacetyl chloride was brominated by direct addition of bromine to the acid chloride at 80°, the product being finally boiled with excess of alcohol, giving *ethyl α-bromophenylacetate*, b. p. 145°/15 mm. This substance reacts with dimethylamine in benzene solution to give *ethyl α-dimethylaminophenylacetate*, $NMe_2 \cdot CHPh \cdot CO_2Et$, b. p. 135°/13 mm., which is readily reduced by sodium in absolute alcohol to *α-dimethyl-amino-α-phenylethanol*, $NMe_2 \cdot CHPh \cdot CH_2 \cdot OH$, b. p. 135—138°/15 mm. and 248—250°/760 mm., solidifying at $-5°$. The following derivatives have been prepared : *hydrochloride*, m. p. 114° ; *picrate*, m. p. 115° ; *gold* salt, m. p. 110°, decomposed on boiling with water, reduced gold being deposited ; *benzoyl* derivative, m. p. 165° ; *morpholone hydrochloride*, m. p. 220°, sparingly soluble in alcohol ; *methiodide*, difficult to crystallise ; *methochloride* [primary *phenylcholine hydrochloride*], $NMe_3Cl \cdot CHPh \cdot CH_2 \cdot OH$, yielding a crystalline *gold* salt and a *picrate*, m. p. 165°. W. G.

Electrolysis in Non-Aqueous Solvents. *o*-Nitrobenzoic Acid Solutions of Potassium *o*-Nitrobenzoate. CARL SCHALL (*Zeitsch. Elektrochem.*, 1913, **19**, 830—833).—Berl (A., 1904, i, 282) showed that the electrolysis of fused organic salts led to results which differed from those obtained from the electrolysis of aqueous solutions of these salts. In the case of the sodium salt of *o*-nitrobenzoic acid melted with its free acid, the product was nitrobenzene, and not 2 : 2'-dinitrodiphenyl as was expected. The author has electrolysed a 15% solution of potassium *o*-nitrobenzoate in *o*-nitrobenzoic acid at 160—170°, using a small porous pot as anode vessel and a beaker as cathode vessel. The anode consisted of 6—7 cms. of platinum wire wound into a spiral, and the cathode was a platinum foil 3 cms. × 7 cms. The electrolysis was carried out by a current of 5 amperes and 50 volts. During the electrolysis an odour of aniline was noticed. On allowing the fusion to cool, the cathode material contained a small quantity of a liquid with an *iso*nitrile odour, and a black substance which dissolved in alkali and acid. The anode vessel contained a little *o*-nitrophenol, a little 2 : 2'-dinitrodiphenyl, and a brown powder of undetermined composition. The experiment of Lilienfeld (D.R.-P. 1902, 147943) was repeated ; by this 2 : 2'-dinitrodiphenyl should be obtained by the electrolysis of copper *o*-nitrobenzoate in aqueous solution. The author is unable to obtain any of this compound either under the specified or any other conditions. J. F. S.

Nitro-*o*-sulphobenzoic Acid and Some of its Derivatives. MARTIN BELL STUBBS (*Amer. Chem. J.*, 1913, **50**, 193—204. Compare Taverne, A., 1906, i, 273).—If *o*-sulphobenzoic acid is treated with a mixture of fuming nitric and concentrated sulphuric acids, the mixture heated until all the nitric acid has been eliminated, and water added to the cooled product, *5-nitro-2-sulphobenzoic anhydride*,

$$NO_2 \cdot C_6H_3 \underset{CO}{\overset{SO_2}{<}} O,$$
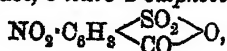
m. p. about 212° (uncorr.), separates in white crystals. *Potassium*

hydrogen 5-*nitro*-2-*sulphobenzoate* crystallises with $1H_2O$, the *lead* salt with $2H_2O$, the *barium* salt with $3H_2O$, and the *copper* salt with $2H_2O$; the *calcium* salt also contains water of crystallisation, whilst the *potassium* salt is anhydrous. On treating the *chloride*,

$$NO_2 \cdot C_6H_3(SO_2Cl) \cdot COCl,$$
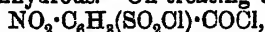
a yellow oil, with dry ammonia, the *sulphinide*,

$$NO_2 \cdot C_6H_3 {<}^{SO_2}_{CO} {>} NH,$$
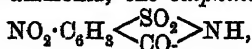
is produced; its *sodium* salt crystallises with $1H_2O$. When the *ethyl* ester of the *chloride*, $NO_2 \cdot C_6H_3(SO_2Cl) \cdot CO_2Et$, obtained as an oil by the action of alcohol on the chloride, is neutralised with barium carbonate, *barium ethyl* 5-*nitro*-2-*sulphobenzoate*,

$$[NO_2 \cdot C_6H_3(CO_2Et) \cdot SO_3]_2Ba, 3H_2O,$$
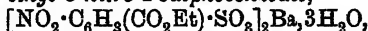
is produced, which forms colourless needles. E. G.

Characterisation of 3 : 5-Dibromotyrosine. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1913, **88**, 124—137).—In view of its importance as a product of hydrolysis of a natural protein (gorgonin), 3 : 5-dibromotyrosine has been studied in detail.

Dibromo-*l*-tyrosine crystallises anhydrous in long, slender needles grouped in voluminous bundles or balls, or with $2H_2O$ in thin plates similar to benzoic acid. It has $[a]_D^{20} + 1 \cdot 3°$.

Dibromo-*dl*-tyrosine crystallises $+ H_2O$ in transparent, four-edged prisms or thick plates. It is nearly twice as soluble in water as the *l*-isomeride. Both forms have m. p. about 245° (much decomp.). They are stable to concentrated sulphuric and hydrochloric acids even on heating. The bromine atoms are removed quantitatively on heating with zinc dust. E. F. A

Ketens. XXIV. Mixed Diphenylacetic Anhydrides and their Decomposition. HERMANN STAUDINGER, E. ANTHES, and H. SCHNEIDER (*Ber.*, 1913, **46**, 3539—3551).—It has been previously shown (Staudinger and Ott, A., 1908, i, 602) that anhydrides of malonic acid decompose when heated, yielding carbon dioxide and ketens. The scope of this method of preparation is greatly limited by the difficulty of preparing such anhydrides, and the authors have therefore investigated the behaviour of mixed anhydrides of malonic and other acids (compare Staudinger and Bereza, A., 1909, i, 83) which can be readily prepared by the action of ketens on malonic acid.

The authors have prepared a series of mixed anhydrides by the action of diphenylketen on derivatives of malonic acid. These are stable, well-crystallised substances which appear to be unimolecular, and thus differ remarkably from the amorphous, polymerised dimethyl- and diethyl-malonic anhydrides (A., 1908, i, 939). An anhydride could not, however, be obtained from malonic acid itself, decomposition occurring in this case at a low temperature with formation of diphenyl-acetic anhydride and brown, resinous products.

The action of heat on the mixed anhydrides causes a primary dissociation into diphenylacetic anhydride and the corresponding malonic anhydride; the latter then loses carbon dioxide to yield the keten. Dimethylketen and diethylketen can be obtained in this

manner from dimethyl- and diethyl-malonic diphenylacetic anhydrides
respectively.   In the latter case, however, small quantities of diphenyl-
keten are also produced.   This is attributed to the partial decom-
position of diphenylacetic anhydride into diphenylketen and diphenyl-
acetic acid, the latter substance also uniting with a portion of the
diethylketen and thus reducing the yield of the latter.   A similar
secondary decomposition occurs quantitatively during the decom-
position of benzylidenemalonic diphenylacetic anhydride, so that the
product of the reaction is diphenylketen instead of the expected
benzylideneketen, whilst the desired ketens were also not obtained
from isopropylidenemalonic diphenylacetic anhydride and dichloro-
malonic diphenylacetic anhydride.   Ethylchloroketen, on the other
hand, was readily obtained from ethylchloromalonic diphenylacetic
anhydride.

The mixed anhydrides are prepared by the addition of diphenyl-
keten to very concentrated solution or suspension of the malonic acid
in absolute ether, reaction being allowed to proceed in an atmosphere
of carbon dioxide.   After a period which depends on the derivative of
malonic acid employed, the mixed anhydride separates in the
crystalline state.   The m. p.'s of the products depend somewhat on the
manner of heating.

Dimethylmalonic diphenylacetic anhydride, $CMe_2(CO \cdot O \cdot CO \cdot CHPh_2)_2$,
has m. p. 91° (decomp.).   When heated at the ordinary pressure, it
yields only small quantities of dimethylketen ; when decomposed in a
vacuum, however, the yield of the latter amounts to 50%.   The liquid,
polymeric compound (Staudinger and Klever, A., 1907, i, 424) of
dimethylketen appears to be formed in small quantity, whilst the
residue consists of almost pure diphenylacetic anhydride.

Diethylmalonic diphenylacetic anhydride, m. p. 94°, when heated in a
vacuum gives a 64% yield of diethylketen ; at a somewhat higher
temperature, diphenylketen is evolved, which is identified by conver-
sion into diphenylacetanilide.

Diphenylacetic anhydride is obtained by the action of diphenylketen
on an ethereal solution of ethylmalonic acid.   The products of the
decomposition of ethylmalonic anhydride have not yet been investigated.

Benzylidenemalonic diphenylacetic anhydride, m. p. 103°, is more
stable than the preceding compounds.   When heated to 180° in a
vacuum, it yields diphenylketen.   Cinnamic and diphenylacetic acids
are obtained by saponification of the residue from the distillation.

iso*Propylidenemalonic diphenylacetic anhydride*, m. p. 101°, decomposes
slowly at its melting point.   When distilled in a vacuum it yields
diphenylketen ; the residue consists of dark brown, pasty mass, which
is probably formed by the rapid polymerisation of the keten and
subsequent decomposition of the polymerisation product.

Dichloromalonic diphenylacetic anhydride, m. p. 74° (decomp.), is an
unstable substance, which slowly decomposes at the ordinary tempera-
ture.   When heated, it yields more than the calculated quantity of
carbon dioxide, and, at a higher temperature, evolves hydrogen chloride.
Dichloroketen has not been isolated.

Ethylchloromalonic acid, m. p. 101—102°, is obtained by boiling an
absolute ethereal solution of ethylmalonic acid with sulphuryl chloride

(compare Conrad and Reinbach, A., 1902, i, 529). It combines with diphenylketen, yielding *ethylchloromalonic diphenylacetic anhydride*, m. p. 95—96°, which, when heated in a vacuum, gives *ethylchloroketen*, CEtClC:O. The latter condenses at −80° to yellow oily drops which in a few minutes, become transformed into a white solid mass. Attempts to obtain the unpolymerised keten at −180° were unsuccessful. In ethereal solutions at −80°, it can only be preserved for a short time. The keten vapours dissolve in ether with a yellow colour, but, after a few seconds, the solution becomes colourless and, on removal of ether, the keten remains as a glassy, somewhat viscous mass, which is no longer completely soluble in the solvent. The keten polymeride is soluble in carbon disulphide, and melts indefinitely at 84—86°. When heated, it decomposes completely, evolving hydrogen chloride and probably chlorobutyryl chloride.

Ethylchloroketen unites with aniline to form chlorobutyranilide.

H. W.

### Conversion of Triphenylmethyl into Triphenylacetic Acid.
ALEXANDER I. GORSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1454—1460). —In consequence of the varying behaviour of heated and non-heated ethereal solutions of magnesium triphenylmethyl chloride towards aromatic aldehydes, Schmidlin (A., 1906, i, 392; 1907, i, 26, 601; 1908, i, 239; this vol., i, 50) assumes the existence of two isomeric organo-magnesium compounds of ω-chlorotriphenylmethane : a normal, stable β-compound, which gives β-benzopinacolin with benzaldehyde, and an unstable quinonoid α-compound, which gives *p*-benzoyltriphenylmethane.

Tschitschibabin (A., 1907, i, 1022) is, however, of the opinion that only one such organo-magnesium compound exists.

Since the experimental results given by Schmidlin in support of his assumption were not obtained under the conditions in which the conversion of the α- into the β-compound actually occurs, the author has investigated the reaction further. By passing dry carbon dioxide into a heated mixture of a benzene solution of triphenylmethyl and the etherate of magnesium iodide, he has succeeded in obtaining good yields of triphenylacetic acid and triphenylmethane; decomposition of the products by means of water failed to give any appreciable amount of triphenylmethyl peroxide. This result is regarded as evidence in favour of Tschitschibabin's view that Schmidlin's α-compound is really a mixture of an ethereal solution of triphenylmethyl with the etherate of magnesium chloride.

T. H. P.

α-*p*-Nitrophenyl-β-hydroxythionaphthen. HERMANN APITZSCH (*Ber.*, 1913, **46**, 3091—3103. Compare A., 1909, i, 46).—*p-Nitrobenzylthiosalicylic acid* [2-*p*-nitrobenzylthiolbenzoic acid],

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot S \cdot C_6H_4 \cdot CO_2H,$$
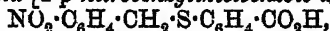
practically colourless, shining prisms, m. p. 215·5° (corr.) after softening at 200°, is prepared by the addition of an alcoholic solution of *p*-nitrobenzyl chloride to an aqueous alcoholic solution of sodium thiosalicylate [*o*-thiolbenzoate] and acidification of the mixture with hydrochloric acid. It dissolves in alkali to a pure yellow solution,

which becomes dark reddish-brown on warming, and from which a definite compound could not be isolated. Small quantities of p-*nitrobenzyl 2-p-nitrobenzylthiolbenzoate*,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot S \cdot C_6H_4 \cdot CO \cdot O \cdot CH_2 \cdot C_6H_4 \cdot NO_2,$$
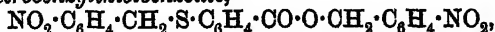
pale yellow crystals, m. p. 194°, are obtained as by-product in the preparation of the acid. Methyl alcohol and hydrochloric acid transform the acid into its *methyl* ester, m. p. 111—112°, which is also obtained by the action of *p*-nitrobenzyl chloride on methyl thiosalicylate in methyl alcoholic solution in the presence of the calculated amount of 2N-potassium hydroxide. When boiled with a methyl alcoholic solution of sodium methoxide and subsequently carefully acidified with acetic acid, the methyl ester is converted into 2-*hydroxy*-1-p-*nitrophenylthionaphthen*, $C_6H_4 \overset{C(OH)}{\underset{S}{<}} C \cdot C_6H_4 \cdot NO_2$, which exists

in a yellow ketonic form, a red enolic form, and as an orange-red mixture. The forms readily pass into one another, so that definite directions for the productions of a definite modification cannot readily be given. The red form, however, which decomposes at 195° after previous softening, is obtained when this crude product is crystallised from aqueous alcohol. From ethyl acetate, chloroform, or glacial acetic acid solution, the yellow keto-form frequently separates in well defined, rhombohedric crystals, usually mixed with the red needles. The mixed form is obtained from solutions of the crude product in benzene, toluene, or xylene in the form of thin, orange-red needles, which are stable and do not become yellow on drying.

In the following experiments the red modification was used. When treated with an equivalent quantity of sodium methoxide in absolute alcoholic solution, the *sodium* salt, $C_{14}H_8O_3NSNa$, blue needles, is obtained. Benzyl chloride in the presence of alkali in aqueous alcoholic or absolute alcoholic solution yields two *benzyl* derivatives, greenish-yellow needles, m. p. 143·5° after softening at 142°, and almost colourless, irregularly formed needles, m. p. 144—145° (corr.), which can be separated by crystallisation from alcohol. A mixture of the two forms melts at 120°. Treatment with ethyl bromide leads to the formation of only one *ethyl* derivative, yellow needles, m. p. 109·5°.

2-*Hydroxy*-1-p-*aminophenylthionaphthen*,

$$C_6H_4 \overset{C(OH)}{\underset{S}{<}} C \cdot C_6H_4 \cdot NH_2,$$
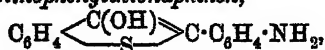
is obtained by the reduction of an alkaline, aqueous alcoholic solution of the nitro-compound by sodium hyposulphite. The substance is purified with difficulty, since it is readily decomposed when warmed in indifferent solvents. It forms white needles, m. p. 130° (corr.), which are sensitive to the action of light and air. The *picrate*, brown needles, begins to decompose at 165°. The salts with mineral acids are generally sparingly soluble and decompose readily. The *oxalate* is converted by nitric acid into a diazonium salt, which couples with R-salt in alkaline solution.

o-Benzylthiolbenzoic acid, needles, m. p. 189°, is formed from benzyl chloride, thiosalicylic acid, and potassium carbonate in boiling aqueous alcoholic solution.

Methyl 2-o-nitrobenzylthiolbenzoate, m. p. 122·5° (corr.), and *methyl* 2-m-*nitrobenzylthiolbenzoate,* rhombohedric plates, m. p. 88—89° (corr.), are obtained from methyl thiosalicylate, 2N-potassium hydroxide, and the requisite nitrobenzyl chloride. They resemble the non-nitrated benzylthiosalicylic acid, in that they do not yield a condensation product when boiled with aqueous alcoholic alkali. H. W.

Vinylphthalimide. MARCEL BACHSTEZ (*Ber.,* 1913, **46,** 3087—3089).—Since phthalylglycyl chloride decomposes when heated into carbon monoxide and chloromethylphthalimide (Gabriel, A., 1908, i, 181), whilst α-phthaliminoisobutyryl chloride decomposes according to the scheme :

$$C_8H_4O_2:N\cdot CMe_2\cdot COCl \longrightarrow CO + HCl + C_8H_4O_2:N\cdot CMe:CH_2$$

(Gabriel, A., 1911, i, 982), the author has examined the action of heat on α-phthalylalanyl chloride (A., 1908, i, 182), and has thereby obtained small quantities of *vinylphthalimide,*

$$C_8H_4O_2:N\cdot CH:CH_2,$$

rhombic plates, m. p. 86°. Attempts to improve the yield by the addition of traces of zinc chloride or aluminium chloride were unsuccessful. The substance unites with bromine to form *phthaliminoαβ-dibromoethane,* needles, m. p. 123—124°, which rapidly decomposes when preserved in the presence of moisture.

A further attempt was made to prepare vinylphthalimide by the abstraction of hydrobromic acid from β-bromoethylphthalimide (compare Johnson and Jones, A., 1911, i, 455) by the action of sodium phenoxide in alcoholic solution. Phenoxyethylphthalimide, m. p. 129—130° (Schmidt, A., 1890, 372), was thereby obtained.

Small quantities of vinylphthalimide were obtained by the action of phosphoric oxide on β-hydroxyethylphthalimide (compare Gabriel, A., 1905, i, 265). H. W.

Toad Venom. HEINRICH WIELAND and FRIEDRICH JOS. WEIL (*Ber.,* 1913, **46,** 3315—3327).—Bufotalin, the poisonous principle of the toad first isolated in an amorphous condition by Faust (A., 1902, i, 446), has now been obtained in the crystalline state. It has the composition $C_{16}H_{24}O_4$, is faintly dextrorotatory and neutral in character. Alkali converts it into the unsaturated bufotalic acid, proving bufotalin to be a lactone. The other two oxygen atoms are present as alcoholic hydroxyl groups. Concentrated hydrogen chloride in the cold eliminates two molecules of water, forming a pale yellow, crystalline compound, $C_{16}H_{20}O_2$, bufotalien. It takes up two atoms of hydrogen in presence of palladium black.

Acetyl chloride in pyridine or warming with acetic anhydride converts bufotalin into a doubly acetylated ether, one hydroxyl group in each molecule being acetylated and the two molecules united through oxygen. Treatment of this diacetyl ether with concentrated hydrochloric acid forms a yellow, strongly unsaturated compound, $C_{18}H_{22}O_3$. The same compound is obtained on heating bufotalein with acetic anhydride, which effects direct acetylation on the carbon. Acetic anhydride is added directly to the C:C complex from which acetic acid is subsequently eliminated.

During the conversion of diacetylbufotalin ether into acetyl bufotalin, the bridge oxygen is first eliminated as water. The single molecules, $-C(OAc){:}CH-$, undergo rearrangement to a saturated diketone, $-CO{\cdot}CHAc-$, which loses water to form the doubly unsaturated monoketone, $-CH{:}CH{\cdot}CH{:}OAc-$. The analogy between bufotalin, $C_{15}H_{22}(OH)_3{\cdot}CO_2H$, and cholic acid, $C_{22}H_{36}(OH)_3{\cdot}CO_2H$, is emphasised. The unsaturated derivatives of both groups give Liebermann's characteristic cholestol reaction with acetic anhydride and sulphuric acid.

Bufotalin is not identical with bufagin, $C_{18}H_{24}O_4$, obtained from the tropical toad by Abel and Macht (A., 1912, ii, 1193).

Bufotalin has m. p. 148° (decomp.), $[\alpha]_D^{20} + 5{\cdot}4°$; it dissolves in concentrated sulphuric acid with an orange-red coloration which becomes deep red on standing and shows a green fluorescence.

Bufotalien forms pale yellow platelets, m. p. 219°. *Acetylbufotalien* separates in lustrous, yellow platelets grouped in rosettes, m. p. 184° (decomp.). *Diacetylbufotalin ether* forms colourless, lustrous platelets, m. p. 254° to a red liquid.   E. F. A.

Action of Chloroacetic Acid on Phenolcarboxylic Acids and Nitrophenols. RICHARD MEYER and CASIMIR DUCZMAL (*Ber.*, 1913, **46**, 3366—3379).—Although the reaction of chloroacetic acid with alcohols and phenols producing ethers according to the equation $R{\cdot}OH + CH_2Cl{\cdot}CO_2H = HCl + OR{\cdot}CH_2{\cdot}CO_2H$ is a fairly general one, it is usually understood that this reaction fails with salicylic acid. The authors find that the reaction can be effected with salicylic acid, although less readily than with most other substances, and, indeed, mere mention of this fact has already appeared (Bogisch, *Diss.*, Stuttgart, 1889), although it has not found its place in the usual literature. The behaviour of the isomeric hydroxybenzoic acids and of the nitrophenols towards chloroacetic acid is also investigated.

The most satisfactory procedure for the reaction with salicylic acid is to dissolve equimolecular quantities of this substance and chloroacetic acid in a concentrated solution of a termolecular quantity of sodium hydroxide. The sodium salt of *o*-carboxyphenoxyacetic acid separates, and the reaction can be completed by heating for some hours on a water-bath. Any salicylic acid in the liberated acid product can be removed by extraction with ether. The yield of *o*-carboxyphenoxyacetic acid, $CO_2H{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CO_2H$, m. p. 190—192°, calculated on the salicylic acid consumed amounts to approximately 80%.

m-Hydroxybenzoic acid, dissolved in sodium hydroxide solution of 35% strength, when gradually treated with chloroacetic acid gave rise to *m*-carboxyphenoxyacetic acid, m. p. 206—207°.

When equimolecular quantities of ethyl chloroacetate and sodium *m*-hydroxybenzoate are heated together in a sealed tube at 170° for thirty hours, *ethyl* m-*hydroxybenzoyloxyacetate* is obtained as a viscous oil, which can be hydrolysed by sodium hydroxide solution at 3° to *m*-*hydroxybenzoyloryacetic acid*,

$$CO_2H{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}OH,$$
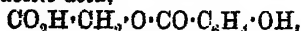
prisms, m. p. 138—140°. On warming with sodium hydroxide solution it is hydrolysed to *m*-hydroxybenzoic acid.

When treated in boiling sodium hydroxide solution (35%) with an equimolecular quantity of chloroacetic acid, *p*-hydroxybenzoic acid is converted into *p*-carboxyphenoxyacetic acid, m. p. 278°.

The action of ethyl chloroacetate on sodium *p*-hydroxybenzoate is similar to the meta-compound and requires similar conditions; the product is an oily *ethyl* ester, which on hydrolysis with cooled sodium hydroxide solution yields p-*hydroxybenzoyloxyacetic acid,*

$$CO_2H \cdot CH_2 \cdot O \cdot CO \cdot C_6H_4 \cdot OH,$$
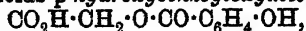
silky needles, m. p. 174—175°.

o-Cresotic acid when treated in sodium hydroxide solution with chloroacetic acid produces 3-*carboxy*-o-*tolyloxyacetic acid*, needles, m. p. 203—204°. In a similar manner, *m*-cresotic acid gives rise to 4-*carboxy*-m-*tolyloxyacetic acid*, nodular aggregates, m. p. 164—165°, whilst the *p*-cresotic acid yields 3-*carboxy*-p-*tolyloxyacetic acid*, leaflets, m. p. 185°.

1 : 2- and 2 : 3-Hydroxynaphthoic acids were likewise applied to this synthetic reaction, sufficient sodium hydroxide being used to just neutralise the acid reagents. The former acid gave rise to 2-*carboxy*-1-*naphthoxyacetic acid*, silky needles, m. p. 206—207°, whilst the 2 : 3-isomeride produced 3-*carboxy*-2-*naphthoxyacetic acid*, leaflets, m. p. 224—225°.

Chloroacetic acid acts quite normally on the sodium salt of 2 : 4-dinitrophenol, but as the product is rather unstable, excess of alkali must be avoided ; the resulting 2 : 4-dinitrophenoxyacetic acid had m. p. 147—148°.

No success attended attempts to obtain a condensation product of chloroacetic acid with picric acid, even when the latter was applied as the silver salt ; as free picric acid and silver chloride were produced, it is probable that the primary product underwent immediate decomposition.

In all the above cases especial attention was given to the yields of the products, and although the interaction of *o*- and *p*-nitrophenols with chloroacetic acid had already been investigated, experiments were performed to determine the yields ; *m*-nitrophenol was found to behave similarly to the others, producing 3-*nitrophenoxyacetic acid*, needles, m. p. 154—155°.

None of the above substances gives a quantitative result ; it is found that the ortho-compounds give by far the poorest yields, and the difficulty of reaction observed with salicylic acid is evidently to be attributed to its ortho-configuration. With the meta- and para-compounds the yields are much better, the para-compounds being the more satisfactory. D. F. T.

The Condensation Product of Methyl 2 : 3-Hydroxynaph-thoate with Benzaldehyde. LEO ROSLAV (*Monatsh.*, 1913, **34**, 1503—1518. Compare Friedl, A., 1910, i, 741 ; also the three follow-ing abstracts).—As Friedl has already shown, the chlorine atom of methyl 1-*a*-chlorobenzyl-2-naphthol-3-carboxylate, the product obtained when hydrogen chloride is passed into a cold mixture of the above

substances, is highly reactive. Many reactions are now described in which this property is exemplified.

On condensation in presence of sodium in benzene, the compound yielded *methyl aβ-diphenylethane-aβ-bis-2-naphthol-3-carboxylate*,

$$C_2H_2Pb_2[C_{10}H_5(OH)\cdot CO_2Me]_2,$$
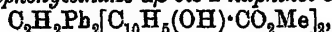
in microscopic prisms, m. p. 227°, which gave violet-red solutions in sulphuric acid. When boiled with *p*-cresol in benzene, it formed *methyl 1-a-p-tolyloxybenzyl-2-naphthol-3-carboxylate*,

$$C_6H_4Me\cdot O\cdot CHPh\cdot C_{10}H_5(OH)\cdot CO_2Me,$$
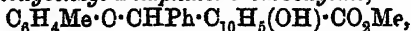
in microscopic leaflets, m. p. 192—193°, whilst thymol yielded *methyl 1-a-thymoxybenzyl-2-naphthol-3-carboxylate*, in yellow, microscopic, rhombic leaflets, m. p. 187—188°.

The chlorine atom in the benzyl group was also replaced by bases, and the following compounds were obtained : from *p*-aminoazobenzene, the *a-benzeneazoanilino*-derivative, slender, orange-yellow needles, m. p. 221°; from carbamide, the *a carbamido*-derivative, only one amino-group reacting, small, faintly yellow prisms, m. p. 194—195°; from benzylamine, the *a-benzylamino*-derivative, long, rectangular plates, m. p. 105—106°, *hydrochloride*, m. p. 172° (decomp.); from piperidine, the *a-piperidino*-derivative, greenish-yellow, m. p. 145—146°, unstable *hydrochloride*, m. p. 174—175°; from phenylhydrazine, the *a-phenylhydrazino*-derivative, lemon-yellow, hard rosettes, m. p. 188°; from ethyl sodiomalonate, the mixed *ester*,

$$CH(CO_2Et)_2\cdot CHPh\cdot C_{10}H_5(OH)\cdot CO_2Me,$$
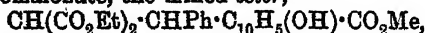
long, yellow prisms, m. p. 130—131°.

It was expected that with pyridine the substance might react in its ketonic form and yield an *o*-quinone, but a *pyridinium chloride*, $C_5H_5NCl\cdot CHPh\cdot C_{10}H_5(OH)\cdot CO_2Me$, was precipitated as a yellow powder, decomp. 162—163°, when the base was added to a solution of the compound in benzene. The aqueous solution, especially with silver oxide, soon deposited methyl 1-a-hydroxy-benzyl-2-naphthol-3-carboxylate (Friedl, *loc. cit.*), and potassium hydroxide gave, in addition, the above ethane derivative. Quinoline behaved similarly, but no pure product could be isolated.

Colour reactions with ferric and stannic chlorides, sulphuric and perchloric acids are described.   J. C. W.

Condensation of *p*-Tolualdehyde with Methyl 2:3-Hydroxy-naphthoate. Marius Rebek (*Monatsh.*, 1913, 34, 1519—1546).— Methyl 2 : 3-hydroxynaphthoate, which, with the ethyl ester, has been crystallographically examined by von Lang, condenses just as readily with *p*-tolualdehyde under the influence of hydrogen chloride or bromide as it does with benzaldehyde. *Methyl 1-a-chloro-p-methylbenzyl-2-naphthol-3-carboxylate*, $C_6H_4Me\cdot CHCl\cdot C_{10}H_5(OH)\cdot CO_2Me$, forms pale yellow, microscopic tablets, m. p. 143—145°, which give various colour reactions with sulphuric and perchloric acids and stannic and ferric chlorides. The *a-bromo*-derivative forms yellow, glittering, flat leaflets, m. p. 157—159°. In the case of hydrogen bromide, a good yield of the condensation product was obtained when molecular quantities of the reacting substances were diluted with ether. From such a solution, hydrogen chloride gave no crystals for some days,

when, finally, a condensation product of the α-chloro-derivative with more ester, namely, *methyl* p-*xylylidenebis*-2-*naphthol*-3-*carboxylate* (p-*tolyl-di*-2-*hydroxy*-3-*carbomethoxynaphthylmethane*),

$$C_6H_4Me\cdot CH[C_{10}H_5(OH)\cdot CO_2Me]_2,$$

was obtained in well-defined prisms, m. p. 218—222°, which crystallised with ½ mol. of chloroform.

On adding water to a cold acetone solution of the α-bromo-derivative, *methyl* 1-α-*hydroxy*-p-*methylbenzyl*-2-*naphthol*-3-*carboxylate*,

$$C_6H_4Me\cdot CH(OH)\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

crystallises in yellow, rhombic leaflets, m. p. 155—158°. This compound tends to condense to an ether, especially in presence of alcohol or hydrochloric acid, or on melting. When the α-chloro-derivative was boiled with moderately strong hydrochloric acid, the same compound, *methyl* αα′-*oxidobis*-1-p-*methylbenzyl*-2-*naphthol*-3-*carboxylate*,

$$O[CH(C_6H_4Me)\cdot C_{10}H_5(OH)\cdot CO_2Me]_2,$$

was obtained in yellow, micro-leaflets, m. p. 216·5—219°. The speed of the action with water was roughly determined at ordinary temperatures.

When warmed with acetic anhydride and sodium acetate, the yellow halogen compounds became colourless, and an amorphous, acetylated derivative, which could not be crystallised, was obtained. Methyl alcohol condensed with the compounds to form *methyl* 1-α-*methoxy*-p-*methylbenzyl*-2-*naphthol*-3-*carboxylate*,

$$C_6H_4Me\cdot CH(OMe)\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

in microscopic prisms, m. p. 178—180·5°. The α-halogen atom in the xylyl group was also replaced by a number of alcohol- and basic radicles, and the following corresponding condensation products obtained : α-*ethoxy*-derivative, stout, microscopic prisms, m. p. 95·5—97·5°; α-*propoxy*-derivative, yellow, microscopic prisms, m. p. 105·5—108·5°; α-*phenoxy*-derivative, faintly yellow prisms, m. p. 175—176°; p-*tolyloxy*-derivative, rectangular plates or leaflets, m. p. 165·5—167°; α-*thymoxy*-derivative, stout, microscopic needles, m. p. 188—189°; α-*anilino*-derivative, pale yellow, m. p. 210—211·5°; α-*phenylhydrazino*-derivative, lemon-yellow needles, decomp. 140°; α-*piperidino*-derivative, silky needles, m. p. 172—173·5°; p-*benzeneazoanilino*-derivative, orange, short prisms, m. p. 210—210·5°, reddened by hydrochloric acid.

Methyl α-chloro-1-p-methylbenzyl-2-naphthol-3-carboxylate was hydrolysed by adding hydriodic acid to a warm solution in acetic anhydride. p-*Methylbenzyl*-2-*naphthol*-3-*carboxylic acid*,

$$C_6H_4Me\cdot CH_2\cdot C_{10}H_5(OH)\cdot CO_2H,$$

formed intensely yellow crystals, m. p. 249—250° (decomp.), and gave a white *silver* salt, decomp. 210°, from which the *methyl* ester, m. p. 137—138°, was prepared. The latter was also present in the product from the above hydrolysis.

Characteristic colour reactions are exhibited by all these compounds.

J. C. W.

Condensation of Anisaldehyde with Methyl 2 : 3-Hydroxynaphthoate. FRITZ WEISHUT (*Monatsh.*, 1913, 34, 1547—1565).— Studies analogous to the foregoing were carried out with anisaldehyde.

Methyl 1-*a-chloro*-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*,

$$OMe \cdot C_6H_4 \cdot CHCl \cdot C_{10}H_5(OH) \cdot CO_2Me,$$

formed yellow prisms, m. p. 171—173°, decomp. 185°, and gave a series of remarkable colour reactions with strong acids, due to the presence of a carbonium valence. Silver sulphate rendered a warm benzene solution violet-red; the colour disappeared on cooling and returned on warming. The *bromo*-analogue had m. p. 162—164°. An attempt to prepare this compound by condensation in methyl alcohol solution gave as a by-product, *methyl anisylidenebis*-2-*naphthol*-3-*carboxylate*, $OMe \cdot C_6H_4 \cdot CH[C_{10}H_5(OH) \cdot CO_2Me]_2$, in pale yellow, microscopic crystals, m. p. 213—215°.

Cold water precipitated from an acetone solution of the halogen derivatives, *methyl* 1-*a-hydroxy*-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*, which formed pale yellow leaflets, m. p. 129—130°. The speed of the reaction with water was measured in the case of the *a*-chlorobenzyl-, *a*-chloro- and *a*-bromo-anisyl compounds of this series, and the influence of the methoxy-group and the halogen atom were determined. The methoxy-group renders the lability of the halogen atom of the order of an ionic reaction, whilst the bromo-compounds are more reactive than the chloro-. Boiling water gave rise to *methyl* *aa'-oxidobis*-1-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*,

$$O[CH(C_6H_4 \cdot OMe) \cdot C_{10}H_5(OH) \cdot CO_2Me]_2,$$
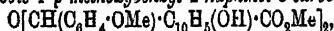
in yellow prisms, m. p. (without crystal solvent) 202—204°.

Methyl alcohol yielded *methyl* 1-*a*-p-*dimethoxybenzyl*-2-*naphthol*-3-*carboxylate*, $OMe \cdot C_6H_4 \cdot CH(OMe) \cdot C_{10}H_5(OH) \cdot CO_2Me$, in pale yellow, glittering tablets, m. p. 176—177°. Ammonia in benzene formed *methyl* *iminobis*-1-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*,

$$NH[CH(C_6H_4 \cdot OMe) \cdot C_{10}H_5(OH) \cdot CO_2Me]_2,$$
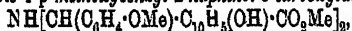
as a yellow substance, m. p. 145—148°. With carbamide in boiling acetone, *methyl* *carbamido-s-bis*-1-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*, $CO[NH \cdot CH(C_6H_4 \cdot OMe) \cdot C_{10}H_5(OH) \cdot CO_2Me]_2$, was obtained as a microcrystalline powder, m. p. 187—189°.

The following *a*-substituted condensation products were also prepared : *a-anilino*-, faint greenish-yellow, microcrystalline powder, m. p. 191—192°; *a*-p-*benzeneazoanilino*-, small, orange needles, m. p. 194—195°; *a-benzylamino*-, faintly yellow crystals, m. p. 107—108°; *a-piperidino*-, pale yellow powder, m. p. 166—167°. The basic substituents, in general, give rise to compounds which react in the enolic form, giving intense colours with ferric chloride, but not with strong acids.

The *a*-hydroxyl and *a*-anilino-groups were replaced by the methoxy-group, merely on boiling the substances concerned with methyl alcohol. Similarly, hydrogen chloride reconverted the ether or the methoxy-compound into the *a*-chloro-derivative.   J. C. W.

Condensation of Methyl 2:3-Hydroxynaphthoate with p- and m-Nitrobenzaldehydes. JOSEF SEIB (*Monatsh.*, 1913, **34**, 1567—1591).—The influence of the nitro-group on the lability of the halogen atom in compounds analogous to the foregoing has been studied. A rough determination of the speed of the decomposition by cold water showed that the compounds were not half as reactive as

the unsubstituted ones, that the *m*-nitro-derivatives were more active than the para-isomerides and that, as before, bromine in the α-position is more labile than chlorine.

Methyl 1-*a-chloro*-p-*nitrobenzyl*-2-*naphthol*-3-*carboxylate*,

$$NO_2 \cdot C_6H_4 \cdot CHCl \cdot C_{10}H_5(OH) \cdot CO_2Me,$$
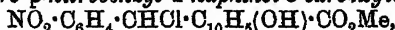
formed pale yellow, glistening prisms, m. p. 227—228·5°. On boiling with water it yielded the α·*hydroxy*-derivative in lemon-yellow prisms, m. p. 188—190°, which gave the α-*acetoxy*-compound, short prisms, m. p. 185—187·5°, on boiling with acetic anhydride. The α-*methoxy*-compound, formed slender, very pale yellow prisms, m. p. 149—150°; the α-*ethoxy*-derivative, long, yellow, rectangular tablets, m. p. 116—117°; the α-*phenoxy*-derivative, white needles, m. p. (with $1\frac{1}{2}$ mols. C_6H_6) 181—181·5°; the α-p-*tolyloxy*-derivative, pale yellow needles, m. p. 180—180 5°; the α-*thymoxy*-derivative, yellow, microscopic prisms, m. p. 208—209°; the α-*anilino*-derivative, glistening, lemon-yellow tablets, with $\frac{3}{4}C_6H_6$, m. p. 197·5—198°, without crystal solvent, pure yellow, m. p. 199—201°, colourless *hydrochloride*, m. p. 168—171°; the α-p-*azo-benzeneanilino*-derivative, long, velvety, dark yellow needles, m. p. 154—156°; the α-*benzylamino*-derivative, long, slender, white needles, m. p. 152—153°; the α-*piperidino*-derivative, yellow, rhombic leaflets, m. p. 176·5—177°. In their colour reactions, as before, the compounds with bases exhibit enolic properties, whereas the ketonic form is more pronounced in the remaining compounds.

Pyridine did not cause the total displacement of chlorine, but yielded the α-*pyridinium chloride*,

$$NO_2 \cdot C_6H_4 \cdot CH(C_5NH_5Cl) \cdot C_{10}H_5(OH) \cdot CO_2Me,$$
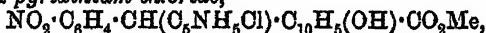
in pale yellow, prismatic tablets, m. p. 110°, which were completely hydrolysed in aqueous solution, especially in presence of silver oxide, to pyridine and the α-hydroxy-compound.

Methyl 1-*a-bromo*-p-*nitrobenzyl*-2-*naphthol*-3-*carboxylate* was obtained in yellow crystals, m. p. 207—208°. Hydriodic acid, however, yielded no crystalline product.

Methyl 1-*a-chloro*-m-*nitrobenzyl*-2-*naphthol*-3-*carboxylate* had m. p. 187—189°, and the *bromo*-analogue formed thin, pale yellow leaflets, with $1C_6H_6$, m. p. 177—178°. *o*-Nitrobenzaldehyde, on the contrary, yielded no definite condensation product with methyl 2 : 3-hydroxy-naphthoate. J. C. W.

Hydroxy-and Dihydroxy-diphenylcarboxylic Acids. MATHÄUS MURDBOVČIĆ (*Monatsh.*, 1913, **34**, 1417—1441).—3 : 3'-Dihydroxy-diphenyl-4 : 4'-dicarboxylic acid, 3-hydroxydiphenyl-4 : 4'-dicarboxylic acid, and several of their derivatives have been prepared.

Dianisidine was diazotised and converted into the nitrile and this was saponified, with difficulty, by boiling for seventy to eighty hours with alcoholic potassium hydroxide. The crude 3 : 3'-*dimethoxydiphenyl-4 : 4'-dicarboxylic acid*, being only sparingly soluble, was converted into the methyl ester and recovered from this by hydrolysis, as a white, microcrystalline powder, m. p. 270—271·5°. The *potassium* salt, $C_{16}H_{21}O_6K_2,2H_2O$, forms long needles from dilute solutions in spirit, and the *silver* salt is a brown, crystalline powder. The *methyl* ester forms white leaflets, m. p. 170—171°. On heating either the ester or

the acid with hydriodic or hydrobromic acid, 3 : 3′-*dihydroxydiphenyl-4 : 4′-dicarboxylic acid* was obtained as a white, amorphous, sparingly soluble powder, m. p. 318° (decomp.). It gives a colourless solution in sulphuric acid, a deep violet coloration with alcoholic ferric chloride, and apparently forms anhydrides under the influence of thionyl chloride. The *methyl* ester forms slender, colourless needles, m. p. 213—215°, and is readily converted into *methyl 3 : 3′-diacetoxydiphenyl-4 : 4′-dicarboxylate*, which crystallises from alcohol in leaflets, m. p. 140—142°.

The methoxy-acid, in contrast to the hydroxy-acid, reacted smoothly with thionyl chloride, forming the *acid chloride*, $C_{16}H_{12}O_4Cl_2$, from a benzene solution of which, ammonia precipitated the *amide*. This forms large needles, $C_{16}H_{16}O_4N_2$,EtOH, from dilute alcohol, m. p. 254—260° (260—261° alcohol-free). On condensing the acid chloride with benzene in presence of aluminium chloride, 3 : 3′-*dihydroxy-4 : 4′-dibenzoyldiphenyl*, $C_{26}H_{18}O_4$, was obtained. The ketone was purified by solution in alkali, reprecipitation by carbon dioxide, heating with hydriodic acid, and crystallisation from alcohol. It forms yellow needles, m. p. 215·5—217·5°, gives a deep yellowish-green, fluorescent solution in sulphuric acid and a reddish-brown coloration with ferric chloride. It was converted by methyl sulphate into 3 : 3′-*dimethoxy-4 : 4′-dibenzoyldiphenyl*, which forms colourless, flat needles, m. p. 156—158°.

As starting material for the preparation of the monohydroxy-compounds, technical ethoxybenzidine was chosen. This was converted into a black, spongy nitrile, which was then hydrolysed as before. Owing to the ready solubility of the acid, however, the crude product could not easily be purified. It was therefore hydrolysed by heating in phenol solution with hydriodic acid, and the crude 3-*hydroxydiphenyl-4 : 4′-dicarboxylic acid* was esterified and recovered by hydrolysis. It forms a white, microcrystalline powder, m. p. 324—325°, crystallises with $1H_2O$ from diluted methyl alcohol, and gives a violet ferric chloride reaction. The *potassium* salt, $C_{14}H_8O_5K_2,H_2O$, and the light brown *silver* salt were prepared. The *methyl* ester forms long, white, glistening needles or leaflets, m. p. 168°, and does not condense with benzaldehyde. *Methyl 3-acetoxydiphenyl-4 : 4′-dicarboxylate* crystallises in very soluble, flat needles, m. p. 119°.

The isomeric mono-esters were prepared according to Wegscheider's directions for hydroxyterephthalic acid (A., 1900, i, 658). Partial hydrolysis of the dimethyl ester with potassium hydroxide yielded 4′-*methyl 4-hydrogen 3-hydroxydiphenyl-4 : 4′-dicarboxylate*, which could be separated from the dicarboxylic acid by benzene, in which the latter is insoluble. It has m. p. 240—241·5° (decomp.), gives a deep violet coloration with ferric chloride, and forms a *potassium* salt. 4-*Methyl 4′-hydrogen 3-hydroxydiphenyl-4 : 4′-dicarboxylate* was obtained in small yield by heating the acid potassium salt with methyl iodide in a sealed tube. It crystallises from benzene in needles, m. p. 215—216°, which give no coloration with ferric chloride.

Schmidt and Schall (A., 1906, i, 23) described 4-hydroxydiphenic acid as a yellow compound. The author also obtained a yellow product,

but on attempting to condense it with benzaldehyde it crystallised as a colourless compound, m. p. 246·5°, the impurity remaining dissolved.

J. C. W.

The Ethers and Esters of Hydroxyquinolphthalein. FRIEDRICH KEHRMANN and RICHARD BERG (*Ber.*, 1913, **46**, 3020—3028).— When hydroxyquinolphthalein in solution in sufficient aqueous sodium hydroxide to form the normal salt is warmed with one and two-third times its weight of methyl iodide, the solution on acidification with acetic acid deposits the *trimethyl ether* (formula I), which frequently
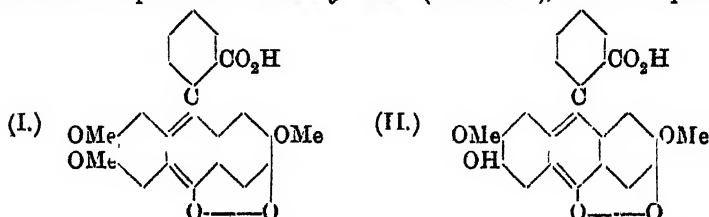
separates from a mixture of benzene and methyl alcohol in a feebly coloured, presumably lactonoid form; this on recrystallisation from methyl alcohol passes into the quinonoid form, orange-yellow, microscopic leaflets, m. p. 257°; the solution in alkali is yellow with a green fluorescence. The mother liquor from which the trimethyl ether has separated contains the sodium salt of the *dimethyl ether* (formula II), and this substance is deposited as the *hydrochloride* on the addition of concentrated hydrochloric acid; the free ether is liberated from its hydrochloride by the action of sodium acetate solution. This dimethyl ether, m. p. 270—271°, crystallises from methyl alcohol in reddish-brown prisms containing 1MeOH; it dissolves in sodium hydrogen carbonate solution, giving the *sodium* carboxylic salt as a yellowish-red solution with a green fluorescence; addition of sodium hydroxide solution causes the formation of the *disodium* salt, with an increase of the fluorescence; *silver* salt, insoluble reddish-brown precipitate.

On saturating a concentrated methyl-alcoholic solution of the trimethyl ether with hydrogen chloride and keeping for several weeks, needles of the *chloride* (formula III) are obtained. By treatment
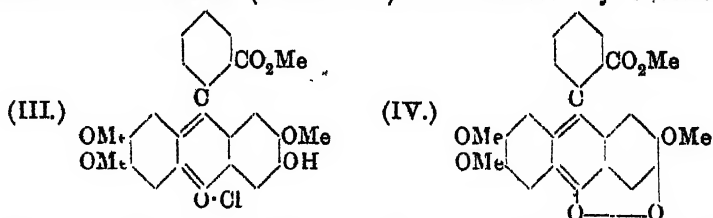

with warm sodium acetate solution, this is converted into the free methyl *ester* of the trimethyl ether (formula IV), which crystallises from a mixture of benzene and methyl alcohol in orange-yellow, iridescent leaflets, m. p. 271—272°.

A similar esterification of the above-mentioned dimethyl ether gives rise to an analogous ester *chloride*, yellow needles, which on decomposition by sodium acetate solution passes into the free *ester* of the dimethyl ether, red crystals, m. p. 248°.

The action of methyl sulphate on a solution of the ester of the trimethyl ether in nitrobenzene solution gave rise to the methyl sulphate salt of the methyl ester of the tetramethyl ether. From this "mixed" sulphate the more ordinary salts were easily obtainable, and their solubility is found to be comparable with those of the corresponding potassium salts; formula V is the *chloride*.

The chloride, *bromide*, and *iodide* are very soluble, the *nitrate*, *chlorate*, *dichromate*, and *persulphate* are moderately soluble, whilst the *perchlorate* and *platinichloride* are sparingly soluble in water. If an aqueous solution of the nitrate is treated in the cold with an excess of
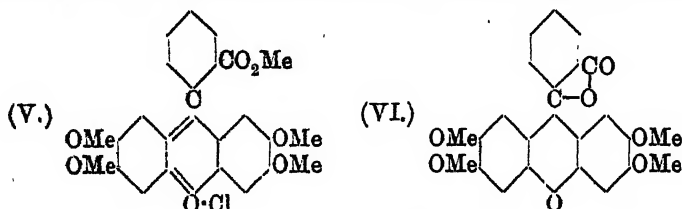
fairly concentrated sodium hydroxide solution, a precipitate is produced, which subsequently redissolves as the *sodium* salt of the tetramethyl ether carboxylic acid; on the addition of acetic acid and warming, the tetramethyl ether lactone (formula VI), colourless prisms, m. p. 202°, is obtained.   D. F. T.

Resorcinolbenzein and Fluorescein. FRIEDRICH KEHRMANN (*Ber.*, 1913, **46**, 3028—3036).—A reply to von Liebig (A., 1912, i, 376; this vol., i, 79, 865). In the case of derivatives of fluorescein with which von Liebig obtained results at variance with those of the author and his collaborators, the substances have been reinvestigated with entire confirmation of the earlier results.

It has already been stated by Fischer and Hepp (A., 1895, i, 291) that the quinonoid dimethyl ether of fluorescein crystallises in two forms, namely, orange-yellow needles and deep red prisms. The difference in the m. p.'s recorded by von Liebig and by Kehrmann and Dengler (A., 1909, i, 249) is due to this dimorphism. Indeed, if a quantity of the orange-yellow needles is heated rapidly to 180°, it melts momentarily and resolidifies to melt again at approximately 194°; under similar treatment the red prisms melt at 208°.

The substance, m. p. 255°, obtained by von Liebig by the action of ammonia solution on the ether-insoluble residue (correctly regarded as trimethylfluorescein chloride) from the reaction product of methyl sulphate and disodium fluorescein, is not a dimethyl ether of fluorescein, but contains almost 2% of nitrogen and probably represents a carbinylimide or a carboxylimide.   D. F. T.

Synthesis of Depsides, Moss Acids, and Tannins. EMIL FISCHER (*Ber.*, 1913, **46**, 3253—3289).—A lecture before the German

Natural Science Congress (compare A., 1908, i, 892; 1909, i, 161, 309; Fischer and Freudenberg, A., 1910, i, 265; 1911, i, 874; 1912, i, 471, 887; Fischer and Hoesch, A., 1912, i, 859, etc.). The following facts are new. Evernic acid is dissolved by an ethereal solution of diazomethane after a time, and converted into the crystalline neutral ester, which is identified as methyl trimethyl-lecanoric acid. The constitution of evernic acid is thus established. Pentasalicyloglucose and the corresponding derivative of caffeic acid have been prepared, also pentacinnamoyl derivatives of α- and β-glucose, galactose, and mannose. *Penta-acetyl mannose* has m. p. 114—116°, $[\alpha]_D^{20} - 24\cdot 8°$.

E. F. A.

Humic Acids. IV. Investigations of Tacke and Süchting EUGEN GULLY (*Bied. Zentr.*, 1913, **42**, 655—659; from *Mitt. K. Bayr. Moorkulturanst.*, 1912, Heft. 5).—A reply to Tacke and Süchting (A., 1912, i, 473), in which the non-existence of humic acids is maintained. Further experiments showed that peat has no action on calcium oxalate; and that bases absorbed by *Sphagna* can be extracted by water free from carbon dioxide. The various results obtained with peat, such as the liberation of iodine from its salts, the inversion of sucrose, and the production of hydrogen from peat and iron are not considered sufficient evidence that humic acids exist.

N. H. J. M.

The Autoxidation of Organic Compounds. I. Autoxidation of Aromatic Aldehydes. HERMANN STAUDINGER [with E. HENE and J. PRODROM (*Ber.*, 1913, **46**, 3530—3535).—It has been previously shown (A., 1911, i, 877) that diphenylketen reacts more readily with methoxy- or dimethylamino-substituted aromatic compounds than with the unsubstituted substances, and similar observations have been made during experiments on the action of oxalyl chloride on carbonyl compounds (A., 1909, i, 905). The authors have therefore been led to the determination of the rate of autoxidation of benzaldehyde and a number of its *p*-substituted derivatives.

Weighed quantities of benzaldehyde, *p*-methoxybenzaldehyde, *p*-hydroxybenzaldehyde, and *p*-dimethylaminobenzaldehyde were heated with an excess of oxygen in closed flasks at 131° and the amount of oxygen absorbed was estimated. In a second series of experiments, a regular stream of oxygen was bubbled through the aldehyde, the course of the reaction being followed by estimation of the acid formed. At 131°, however, dimethylaminobenzoic acid readily evolved carbon dioxide; a temperature of 80° was found suitable. The results show that *p*-dimethylaminobenzaldehyde is much less autoxidisable than anisaldehyde, which, however, is less affected than benzaldehyde. This is inexplicable on Engler and Weissberg's hypothesis that the primary product during autoxidation is formed by the addition of a molecule of oxygen to the unsaturated carbonyl group; it is, however, to be expected if Baeyer and Villiger's supposition is adopted that the addition of the oxygen molecule is accompanied by dissociation of the hydrogen atom, $\text{Ph·C}\!\!<^O_H + \text{O·O} \longrightarrow \text{Ph·C}\!\!<^O_{O·O·H}$ (A., 1900, i, 437).

If Staudinger's views as to the asymmetric nature of the intermediate compound are accepted, the hydrogen atom would be more firmly attached to the strongly unsaturated carbonyl group of p-dimethylaminobenzaldehyde than to the relatively saturated carbonyl group of benzaldehyde, and therefore less capable of addition to the oxygen molecule. From this point of view, o-methoxybenzaldehyde should be the least readily, and m-methoxybenzaldehyde the most readily, autoxidisable of the three methoxybenzaldehydes, and this is shown to be actually the case.

Anti-auxochrome groups weaken the unsaturated character of the carbonyl group, and should therefore increase the mobility of the hydrogen atom and the tendency of the substance to autoxidation. p-Nitrobenzaldehyde, which should thus be readily autoxidised, absorbs little oxygen, since it is speedily resinified. The problem was, however, investigated by the introduction of acyl groups into amino- and hydroxy-groups. Acetoxybenzaldehyde, in contrast with hydroxy- and methoxy-benzaldehyde, was found to be almost as readily autoxidised as benzaldehyde.   H. W.

The Autoxidation of Organic Compounds. II. Relationships between Autoxidation and Benzoin Formation. HERMANN STAUDINGER [with E. HENE] (*Ber.*, 1913, **46**, 3535—3538). —If the possibility of formation of intermediate products be disregarded, the formation of benzoin derivatives from aldehydes is comparable with the autoxidation of the latter substances; in the one case, addition of the aldehyde to the carbonyl group occurs, in the other to the oxygen molecule (compare preceding abstract). A benzoin will only be readily produced, therefore, from an aldehyde which contains a relatively unsaturated carbonyl group and a relatively mobile hydrogen atom; thus, dimethylaminobenzaldehyde does not yield a benzoin, since, although the carbonyl group is strongly unsaturated, the hydrogen atom lacks mobility. Favourable conditions for benzoin formation are found in benzaldehyde, anisaldehyde, and p-chlorobenzaldehyde (compare Hantzsch and Glover, A., 1907, i, 538). From this point of view, mixed benzoin derivatives should be obtainable from a pair of aldehydes if the one possesses a sufficiently mobile hydrogen atom, the other a sufficiently unsaturated carbonyl group; the condensation products of p-dimethylaminobenzaldehyde and p-chlorobenzaldehyde with benzaldehyde are described.

p-*Dimethylaminobenzoin*, $NMe_2 \cdot C_6H_4 \cdot CH(OH) \cdot COPh$, m. p. 163—164°, is obtained in 86% yield when a solution of benzaldehyde and p-dimethylaminobenzaldehyde in alcohol is boiled with an aqueous solution of potassium cyanide. The constitution of this substance is deduced from the fact that it condenses with dimethylaniline in the presence of phosphoryl chloride to yield *benzoyltetramethyldiaminodiphenylmethane*, $COPh \cdot CH(C_6H_4 \cdot NMe_2)_2$, pale yellow needles, m. p. 162—164°, which are readily oxidised to a blue dye. Oxidation with Fehling's solution converts p-dimethylaminobenzoin into p-*dimethylaminobenzil*, yellowish-green crystals, m. p. 115—116°.

Under similar conditions, p-dimethylaminobenzaldehyde condenses

with p-chlorobenzaldehyde to yield p-*chloro*-p'-*dimethylaminobenzoin*, m. p. 127—128°.

Benzaldehyde and anisaldehyde, as also chlorobenzaldehyde and anisaldehyde, appear to yield mixed benzoins. A uniform product could not be isolated. Probably a mixture of benzoins is formed in each case which cannot be separated.

Attempts to prepare benzoins from aromatic and aliphatic aldehydes were unsuccessful. H. W.

The Existence of Mandelaldehyde in Aqueous Solution. W. LLOYD EVANS and CHARLES RAYMOND PARKINSON (*J. Amer. Chem. Soc.*, 1913, 35, 1770—1774. Compare this vol., i, 173).—It is already known that, whereas lactaldehyde is incapable of existence in water at 100° (Nef, A., 1905, i, 3), it is sufficiently stable in water at the ordinary temperature to be studied experimentally (Wohl and Lange, A., 1908, i, 943). Nef has shown that mandelaldehyde also cannot exist in water at 100°, and the present investigation demonstrates that it cannot exist even in the presence of cold aqueous alcohol or of dilute sulphuric acid.

Dibromoacetophenone was converted successively into phenylglyoxal acetal, $CHBz(OEt)_2$, and mandelaldehyde acetal, $CH(OEt)_2 \cdot CHPh \cdot OH$. The last-named substance was found to undergo hydrolysis, yielding benzoylcarbinol, $CH_2Bz \cdot OH$, when suspended in $N/20$-sulphuric acid at 0°, when suspended in water at 0°, or even when exposed to the moisture of the atmosphere. D. F. T.
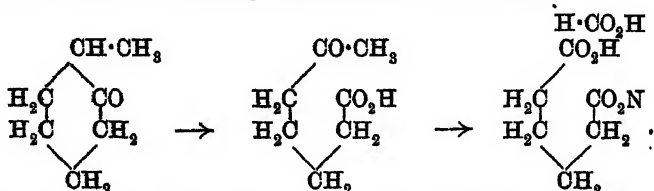
6-Aminopiperonal. AUGUSTE RILLIET and L. KREITMANN (*Compt. rend.*, 1913, 157, 782—784).—Various unsuccessful attempts have been made to prepare the above substance by reduction of 6-nitropiperonal (compare Haber, A., 1891, 704; Friedländer and Schreiber, A., 1895, i, 524). The authors have succeeded by first protecting the aldehyde group.

6-Nitropiperonal condenses readily with various amines to give the corresponding piperonylidene derivatives, of which the following have been prepared : 6-*nitropiperonylidene*-p-*toluidine*, yellow needles, m. p. 121·5°; 6-*nitropiperonylidene*-p-*anisidine*, golden-yellow plates, m. p. 125·5°, and 6-*nitropiperonylidene*-o-*toluidine*, yellow needles, m. p. 128°. All of these are readily reduced in boiling alcoholic solution by sodium sulphide to the corresponding *amino*-compounds, having respectively m. p.'s 134·5°, 162°, and 106°. The hydrolysis of the two latter compounds has not given the desired results, being only brought about with difficulty, but 6-aminopiperonylidene-p-toluidine is readily hydrolysed by prolonged boiling with dilute aqueous alkali, giving 6-*aminopiperonal*, brilliant yellow prisms, m. p. 107°, dissolving in acids to a bright red solution. From it the following derivatives have been prepared : the *mercurichloride*, white needles, decomposing at 135°; a *platinichloride*, a red, amorphous powder, decomposing suddenly on heating ; 6-*benzoylaminopiperonal*, pale yellow needles, m. p. 187·5°; 6-*acetylaminopiperonal*, long, white needles, m. p. 161°, yielding a *phenylhydrazone*, white needles, m. p. 205°, and 6-*aminopiperonalphenylhydrazone*, m. p. 222° (decomp.). W. G.

Chemical Action of Light. XXVII. Autoxidation. V. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1913, **46**, 3077—3084; *Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 339—348).—The action of oxygen and light on acetone, *cyclo*hexanone, the three methyl*cyclo*-hexanones, and methylheptenone has been studied. Except in the cases of acetone and methylheptenone (A., 1910, i, 496), the products obtained are due to the combined effect of autoxidation and hydrolysis (compare A., 1908, i, 277).

Acetone yields formaldehyde and acetic acid, whilst *cyclo*hexanone gives hexoic and adipic acids.

1-Methyl*cyclo*hexan-2-one yields *n*-heptoic acid (œnanthoic acid), adipic acid, and acetylvaleric acid, together with traces of aldehyde, the main reaction proceeding in accordance with the scheme :

$$
\begin{array}{ccc}
\text{CH·CH}_3 & \text{CO·CH}_3 & \begin{array}{c}\text{H·CO}_2\text{H}\\ \text{CO}_2\text{H}\end{array}\\
\underset{\text{H}_2\text{C}}{\diagdown}\underset{\text{CO}}{\diagup} & \underset{\text{H}_2\text{C}}{\diagdown}\underset{\text{CO}_2\text{H}}{\diagup} & \underset{\text{H}_2\text{C}}{\diagdown}\underset{\text{CO}_2\text{N}}{\diagup}\\
\underset{\text{H}_2\text{C}}{}\quad\underset{\text{CH}_2}{} \rightarrow & \underset{\text{H}_2\text{C}}{}\quad\underset{\text{CH}_2}{} \rightarrow & \underset{\text{H}_2\text{C}}{}\quad\underset{\text{CH}_2}{}\ \cdot\\
\underset{\text{CH}_2}{\diagup\diagdown} & \underset{\text{CH}_2}{\diagup\diagdown} & \underset{\text{CH}_2}{\diagup\diagdown}
\end{array}
$$

δ-Acetylvaleric acid has m. p. 31—33°, whilst the semicarbazone melts at 147°. Wallach gives the m. p.'s about 50° and 144—146° respectively (A., 1904, i, 425).

1-Methyl*cyclo*hexan-3-one is less affected than the 1 : 2-derivative, and gives a heptoic acid, b. p. 215—216°, which must have the constitution CH$_2$Me·CH$_2$·CHMe·CH$_2$·CO$_2$H, a dibasic acid, m. p. 97°, identical with the corresponding compound from 1 : 4-methyl*cyclo*-hexanone, and hence having the formula

CO$_2$H·CH$_2$·CH$_2$·CHMe·CH$_2$·CO$_2$H,
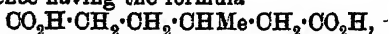
and a lactone which could not be prepared in the pure state.

1-Methyl*cyclo*hexan-4-one gives γ-methylhexoic acid, the above-mentioned dicarboxylic acid and the lactone corresponding with the hydroxy-acid. The latter could not be obtained in a pure condition.

Methylheptenone yields carbon dioxide, acetone, formic acid, acetic acid, and lævulic acid, together with a ketoglycol consisting mainly of the compound OH·CMe$_2$·CH(OH)·CH$_2$·CH$_2$·CO·CH$_3$, possibly mixed with the hydroxydiketone, OH·CMe$_2$·CO·CH$_2$·CH$_2$·CO·CH$_3$. Crystalline derivatives could not be obtained, but the identity of the product follows from its conversion by boiling dilute sulphuric acid into β-methylheptane-γζ-dione, CHMe$_2$·CO·CH$_2$·CH$_2$·CO·CH$_3$, and identification of the semicarbazone and dioxime of the latter with the similar compounds obtained by the oxidation of methylheptenone with potassium permanganate (compare Harries, A., 1902, i, 345). The autoxidation of methylheptenone in light proceeds mainly, therefore, according to the scheme : CMe$_2$:CH·CH$_2$·CH$_2$·CO·CH$_3$ →

OH·CMe$_2$·CH(OH)·CH$_2$·CH$_2$·CO·CH$_3$ →

OH·CMe$_2$·CO·CH$_2$·CH$_2$·CO·CH$_3$ →

CH$_3$·CO·CH$_3$ + CO$_2$H·CH$_2$·CH$_2$·CO·CH$_3$,
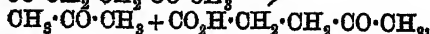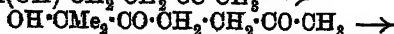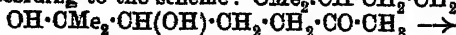
the acetic and formic acids, as probably also the carbon dioxide, being formed by a partial further oxidation of the acetone.   H. W.

Alkylation of 3- and 4-Methyl*cyclo*hexan-3- and 4-ones by means of Sodamide. ALBIN HALLER (*Compt. rend.*, 1913, **157**, 737—743).—Methyl*cyclo*hexan-3- and 4-one not only undergo methylation and allylation under the influence of sodamide, but also ethylation. During the latter reaction condensation of the product on itself is much more pronounced than with the methyl and allyl derivatives. Further, a comparative study of the alkylation of the three methyl*cyclo*hexanones shows that this condensation is much more pronounced the more remote the methyl group is from the ketonic group, and attains its maximum with *cyclo*hexanone itself.

Starting with 1-methyl*cyclo*hexan-3-one, ethyl iodide yields, in ethereal solution in the presence of sodamide, 1-methyl-4-ethyl*cyclo*hexan-3-one (compare A., 1905, i, 214, and Wallach, this vol., i, 482) and 1-*methyl*-2 : 4-*diethylcyclohexan-3-one*, b. p. 216—219°/760 mm., D_4^{17} 0·9061, n_D^{17} 1·4577, together with about 22% of the condensation product. Subsequent successive ethylation of this diethyl derivative furnishes :

1-*Methyl*-2 : 2 : 4-*triethylcyclohexan-3-one*, b. p. 242—244°/770 mm., D_4^{23} 0·9077, n_D^{23} 1·4609.

1-*Methyl*-2 : 2 : 4 : 4-*tetraethylcyclohexan-3-one*, b. p. 266—270°/770 mm., D_4^{20} 0·9358, n_D^{20} 1·4697, having an odour resembling menthone.

1-Methyl*cyclo*hexan-4-ol, b. p. 173—173·5°/760 mm., D_4^{20} 0·9170, n_D 1·4573, obtained by the hydrogenation of *p*-cresol, on oxidation with chromic acid yields 1-methyl*cyclo*hexan-4-one, b. p. 170°/760 mm., D_4^{20} 0·9132, n_D^{20} 1·4458. This ketone on successive methylation under the prescribed conditions with methyl iodide yields :

1 : 3-Dimethyl*cyclo*hexan-4-one (compare Wallach, *loc. cit.*).

1 : 3 : 5-*Trimethylcyclohexan-2-one*, b. p. 184—185°/748 mm., D_4^{20} 0·8992, n_D^{20} 1·4458.

1 : 1 : 3 : 5-*Tetramethylcyclohexan-2-one*, b. p. 190—191°/753 mm., D_4^{20} 0·8903, n_D^{20} 1·4459.

1 : 1 : 3 : 3 : 5-*Pentamethylcyclohexan-2-one*, b. p. 196—198°, D_4^{20} 0·8828, n_D^{20} 1·4461.

Successive introduction of a methyl group produces a regular rise in the boiling point of 6° to 7°, and a steady diminution in the density, whilst the refractive index remains practically constant.

The pentamethyl ketone on hydrogenation with sodium in absolute alcohol yields 1 : 1 : 3 : 3 : 5-*pentamethyl*cyclohexan-2-ol, b. p. 203°/760 mm., D_4^{20} 0·8929, n_D^{20} 1·4581, a viscous liquid having an odour resembling that of eugenol.

Progressive ethylation of 1-methyl*cyclo*hexan-4-one similarly yields :

1-*Methyl*-3-*ethylcyclohexan-4-one*, b. p. 196—198°/761 mm., D_4^{20} 0·8996, n_D^{20} 1·4494, having an odour of menthone.

1-*Methyl*-3 : 5-*diethylcyclohexan-4-one*, b. p. 216—218°/765 mm., D_4^{20} 0·9023, n_D^{20} 1·4562, its odour being identical with that of menthone.

1-*Methyl*-3 : 3 : 5-*triethylcyclohexan-4-one*, b. p. 237—240°/758 mm., D_4^{20} 0·9047, n_D^{20} 1·4615.

1-*Methyl*-3 : 3 : 5 : 5-*tetraethylcyclohexan-4-one*, b. p. 258—262°/760 mm., D_4^{20} 0·9301, n_D^{20} 1·4675 : a viscous liquid with an odour of turpentine. W. G.

5-Acetylamino-2-hydroxyacetophenone and its Derivatives.
FRANZ KUNCKELL (*Ber. Deut. pharm. Ges.*, 1913, **23**, 472—490. Compare A., 1900, i, 663; 1911, i, 990; 1912, i, 268).—2-Hydroxy-5-acetyl-aminoacetophenone, $NHAc \cdot C_6H_3(OH) \cdot COMe$ (compare Kunckell and Hammerschmidt, this vol., i, 1204), is prepared by the gradual addition of aluminium chloride in bright sunlight to a solution of phenacetin in anhydrous carbon disulphide and acetyl bromide (Schmidt, *Diss.*, 1900) or acetyl chloride (Dirk*, *Diss.*, 1906). It forms monoclinic crystals, m. p. 165°. Concentrated hydrochloric acid converts it into 5-*amino-2-hydroxyacetophenone*, yellowish-green needles, m. p. 105°, the *hydrochloride*, white leaflets, m. p. 155° (decomp.), and *sulphate*, m. p. 150°, of which are also described. The *phenylhydrazone* of 2-hydroxy-5-acetylaminoacetophenone forms small, yellow needles, m. p. 107°, whilst the *oxime*, white needles, has m. p. 160°; the nitro-derivative, $C_{10}H_{10}O_5N_2$, yellow needles, m. p. 170°, is obtained by the gradual addition of concentrated nitric acid to a well-cooled solution of the substance in glacial acetic acid.

When treated with a solution of sodium ethoxide in absolute alcohol, 2-hydroxy-5-acetylaminoacetophenone yields the corresponding *sodium* derivative, lemon-yellow leaflets, m. p. 225° (decomp.), which, when heated with ethyl iodide and ethyl alcohol, is converted into 5-*acetyl-amino-2-ethoxyacetophenone*, white needles, m. p. 155° (*phenylhydrazone*, brown needles, m. p. 180°; *mononitro*-derivative, yellowish-red needles, m. p. 125°). Attempts to prepare the substance directly by the action of acetyl chloride and aluminium chloride on phenacetin were unsuccessful, the ethyl group being invariably eliminated. Boiling hydrochloric acid converts it into 5-*amino-2-ethoxyacetophenone hydrochloride*, m. p. 215°.
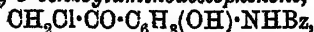
ω-*Chloro-2-hydroxy-5-acetylaminoacetophenone*,
$$CH_2Cl \cdot CO \cdot C_6H_3(OH) \cdot NHAc,$$
yellow needles, m. p. 190°, is prepared by the gradual addition of aluminium chloride in sunlight to a solution of phenacetin and chloro-acetyl chloride in carbon disulphide. The free *base*, yellowish-green needles, has m. p. 135°; *hydrochloride*, white leaflets, m. p. 210° (decomp.). The *oxime* of 2-hydroxy-5-acetylamino-ω-chloroacetophenone has m. p. 195°.

ω-*Chloromononitro-2-hydroxy-5-acetylaminoacetophenone*, yellow needles, m. p. 160°, is obtained by the gradual addition of concentrated nitric acid to a well cooled solution of ω-chloro-2-hydroxy-5-acetylamino-acetophenone in glacial acetic acid. The *oxime* has m. p. 230° (decomp.). The free *base* forms red needles, m. p. 145° (decomp); the *hydrochloride* of the latter decomposes, without melting, at 210°.

ω-*Chloro-2-hydroxy-5-benzoylaminoacetophenone*,
$$CH_2Cl \cdot CO \cdot C_6H_3(OH) \cdot NHBz,$$
m. p. 203°, is prepared by the action of benzyl chloride on an alcoholic solution of ω-chloro-5-amino-2-hydroxyacetophenone. The corresponding *benzoate* has m. p. 166—167°; the *oxime*, m. p. 197°. The *mononitro*-derivative, yellow needles, m. p. 190° (decomp.), is obtained by nitrating the benzoyl derivative in glacial acetic acid solution.

ω-Chloro-5-amino-2-hydroxyacetophenone couples with a diazotised

solution of aniline, yielding a *diazoamino*-compound,

$$CH_2Cl\cdot CO\cdot C_6H_3(OH)\cdot NH\cdot N_2Ph,$$
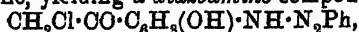
unstable, golden-yellow crystals, m. p. 127°. Attempts to diazotise the base led to the isolation of a *compound* (annexed formula), which explodes without melting at 140°. This substance is decomposed by boiling water, but a pure substance could not be isolated from the product.
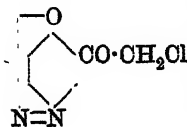
The *phenylurethanes* of ω-chloro-2-hydroxy-5-acetyl-aminoacetophenone and of ω-chloro-5-amino-2-hydroxyacetophenone have m. p.'s 139° and 204° respectively.

The action of phenylhydrazine at a temperature not exceeding 120° on ω-chloro-2-hydroxy-5-acetylaminoacetophenone leads to the formation of the *substance*, $NHAc\cdot C_6H_3(OH)\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh$, needles, m. p. 223°. If the reaction is carried out at a higher temperature and with a relatively smaller quantity of phenylhydrazine, a *substance*, m. p. 247°, is obtained, which has not been completely investigated owing to lack of material. Phenylhydrazine reacts with ω-chloro-5-amino-2-hydroxyacetophenone in a similar manner, yielding the *hydrochloride* of the osazone,

$$HCl,NH_2\cdot C_6H_3(OH)\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh;$$
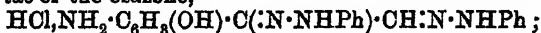
the pure *osazone*, m. p. 205°, is unstable. H. W.

ε-**Aminoketones.** KARL A. BÖTTCHER (*Ber.*, 1913, 46, 3158—3167).—The salts of several benzene-substituted ε-aminoketones have been prepared. Like the simple phenyl ε-aminoamyl ketone in contrast to methyl ε-aminoamyl ketone (Gabriel, A., 1909, i, 492), the new bases do not lose water to form heptacyclic imines, but unlike those simple amines, they yield no definite products under the influence of reducing agents, but are usually unaffected.

Benzoyl-leucine was converted into the chloride, and this condensed with toluene in presence of aluminium chloride. The new benzoyl derivative could not be purified, but was hydrolysed by means of fuming hydrochloric acid in a sealed tube and converted into *tolyl ε-aminoamyl ketone hydrochloride*, $C_{18}H_{20}ONCl$. This salt crystallises in rhombohedra, m. p. 163°, and forms a *platinichloride*, orange-yellow, crystalline powder, m. p. 211°, an *aurichloride*, sulphur-yellow rhombohedra, m. p. 114—116°, and a *picrate*, yellow, jagged crystals, m. p. 148°. The yield of the base was only 18%, but was raised to 41·5% by employing the phthalyl derivative in the condensation. For this purpose, benzoyl-leucine was hydrolysed with fuming hydrochloric acid, the resulting ε-aminohexoic acid was heated with phthalic anhydride, and then converted into ε-phthaliminohexoyl chloride by means of phosphorus pentachloride. On condensation with toluene, the *phthalimino*-derivative, $C_8H_4O_2:N\cdot[CH_2]_5\cdot CO\cdot C_7H_7$, was obtained in well-defined prisms, m. p. 134°. The phthalamino-acid was then prepared by boiling the imide with potassium hydroxide and precipitating with acid, and was finally hydrolysed in a sealed tube. Free *tolyl ε-aminoamyl ketone*, $NH_2\cdot[CH_2]_5\cdot CO\cdot C_7H_7$, was obtained as a colourless oil, b. p. 185—189°/15 mm., m. p. 39—40°, with a basic odour and

strongly alkaline reaction. The *benzenesulphonamide*,

$$C_7H_7 \cdot CO \cdot [CH_2]_5 \cdot NH \cdot SO_2Ph,$$
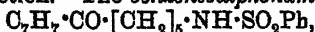
formed long, rectangular tablets, m. p. 135—136°. Like the sulphonyl derivative of heptylamine (Marckwald, A., 1900, i, 149) and like *ε - benzoylamylbenzenesulphonamide* [*benzenesulphonyl- ε - aminohexo - phenone*], $COPh \cdot [CH_2]_5 \cdot NH \cdot SO_2Ph$, which was prepared in rhombic tablets, m. p. 84—85°, from ε-benzoylamylamine [ε-aminohexophenone], it did not dissolve in alkalis, but was changed into oily drops on boiling with 33% potassium hydroxide.

ε-Phthaliminohexoyl chloride was also condensed with anisole. The *phthalimino*-derivative, $C_8H_4O_2 \cdot N \cdot [CH_2]_5 \cdot CO \cdot C_7H_7O$, was obtained in leaflets, m. p. 104°, and converted into the *hydrochloride* of ε-*p-methoxy-benzoylamylamine* (ε-*anisoylamylamine*) [p-*anisyl* ε-*aminoamyl ketone*], $OMe \cdot C_6H_4 \cdot CO \cdot [CH_2]_5 \cdot NH_2,HCl$, which crystallised in thin leaflets, m. p. 166°, and formed a *platinichloride*, sparingly soluble, pale orange, hexagonal leaflets, m. p. 212°; an *aurichloride*, long, orange-yellow rhombohedra, m. p. 118°, and a *picrate*, yellow leaflets, m. p. 135°. The oily base yielded a *phenylthiocarbamide*,
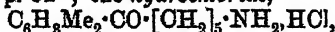
$$C_{13}H_{17}O_2 \cdot NH \cdot CS \cdot NHPh,$$
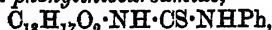
small tablets, m. p. 123°, and a *benzenesulphonamide*, prisms, m. p. 142°.

The following derivatives of ε-*o*-xyloylamylamine [*o*-xylyl ε-amino-amyl ketone] were also prepared : the *phthalimino*-derivative,

$$C_8H_4O_2 \cdot N \cdot C_{14}H_{19}O,$$
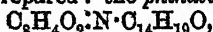
in long needles, m. p. 92°; the *hydrochloride*,

$$C_6H_3Me_2 \cdot CO \cdot [CH_2]_5 \cdot NH_2,HCl,$$

long leaflets, m. p. 122°; *platinichloride*, pale orange leaflets, m. p. 214°; *aurichloride*, thin, lemon-yellow leaflets, m. p. 129°; *picrate*, jagged leaflets, m. p. 142°. The corresponding derivatives of *m*-xylyl ε-aminoamyl ketone are as follows : *phthalimino*-compound, lanceolate crystals, m. p. 71°; *hydrochloride*, hygroscopic needles, m. p. 88—90°; *platinichloride*, very slender, pale orange needles, m. p. 208°; *auri-chloride*, yellow, rectangular, thick tablets, m. p. 99°; *picrate*, small, rectangular, yellow tablets, m. p. 136°. The following derivatives of *p*-xylyl ε-aminoamyl ketone were also prepared : *phthalimide*, needles, m. p. 82°; *hydrochloride*, hexahedra, m. p. 86—87°; *platinichloride*, orange-yellow needles, m. p. 206°; *aurichloride*, thin, yellow leaflets, m. p. 125°; *picrate*, branched needles, m. p. 122°.

Derivatives of ε-3 : 4-dimethoxybenzoylamylamine [veratryl ε-amino-amyl ketone] are also described : *phthalimide*, tufted needles, m. p. 147°; *hydrochloride*, $(OMe)_2C_6H_3 \cdot CO \cdot [CH_2]_5 \cdot NH_2,HCl$, small, slender needles, m. p. 106°; *platinichloride*, orange-yellow, slender, branched needles, m. p. 205°; *aurichloride*, ochreous needles, m. p. 165°. The following derivatives of 2 : 4-dimethoxyphenyl ε-aminoamyl ketone were also prepared : *phthalimide*, long needles, m. p. 117°; *hydro-chloride*, tufted leaflets, m. p. 151—152°; *picrate*, tufted prisms, m. p. 167°; *platinichloride*, orange-yellow, flat needles, m. p. 220°; *auri-chlorides*, $C_8H_9O_2 \cdot CO \cdot [CH_2]_5 \cdot NH_2,HCl,2AuCl_3$, from an aqueous solution, yellow leaflets, m. p. 96°, or

$$C_8H_9O_2 \cdot CO \cdot [CH_2]_5 \cdot NH_2,HCl,AuCl_3,H_2O,$$
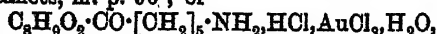
from warm 50% acetic acid, orange-yellow prisms, m. p. 96°. Finally,

the following derivatives of 2 : 5-dimethoxyphenyl ε-aminoamyl ketone are described : *phthalimide*, lanceolate crystals, m. p. 108—109°, which was largely resinified on hydrolysis ; *hydrochloride*, yellowish-green, long needles, m. p. 109° ; *picrate*, yellow rhombohedra, m. p. 151° ; the platini- and auri-chlorides are unstable.   J. C. W.

Action of Heat on Ketoximes. ARTHUR KÖTZ and O. WUNSTORF (*J. pr. Chem.*, 1913, [ii], **88**, 519—530. Compare Angeli and Alessandri, this vol., i, 983).—When heated in the absence of air, ketoximes, which do not distil or sublime without change, undergo decomposition in one of two ways : (1) into ketones, nitrogen, and ammonia: $3CR_2:N\cdot OH \longrightarrow 3COR_2 + N_2 + NH_3$; (2) into nitriles and aldehydes or alcohols :

$$OH\cdot N:CPh\cdot CH_2Ph \longrightarrow CNPh + CH_2Ph\cdot OH$$
$$OH\cdot N:CPh\cdot CHPh\cdot OH \longrightarrow CNPh + C_6H_5\cdot CHO + H_2O.$$
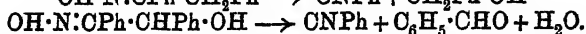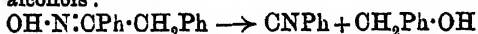
Acetoxime and *cyclo*hexanoneoxime distil without change under ordinary pressure ; at 210—216°, acetoxime decomposes into ammonia, methane, and a mixture of bases, not identified.

When heated in an atmosphere of carbon dioxide, benzophenone-oxime yields benzophenone, nitrogen, and ammonia. Under diminished pressure, acetophenoneoxime may be distilled unchanged, but at ordinary pressures is resolved into acetophenone and ammonia.

Deoxybenzoin decomposes explosively at 270°, yielding benzonitrile, lophine, and benzyl alcohol. At 240°, α-benzoinoxime yields lophine, benzaldehyde, and benzonitrile, whilst oximinocamphor gives rise to camphoric anhydride and αε-dimethyl-Δᵃ-heptenonitrile (Tiemann, A., 1901, i, 18).

4-Oximino-1-methyl*cyclo*hexan-3-one (Takens, *Diss.*, Göttingen, 1910), m. p. 158—159° or 171°, accordingly as it is slowly or rapidly heated, undergoes complete decomposition when heated in an atmosphere of carbon dioxide above its m. p.   F. B.

Polychromic Salts of Oximino-ketones. ISRAEL LIFSCHITZ (*Ber.*, 1913, **46**, 3233—3250).—Additional information as to the constitution of chromoisomerides is given by the study of the electrical conductivity of polychromic salt solutions. Oximinodimethyldihydro-resorcinol, $OMe_2{<}{}^{CH_2\cdot CO}_{CH_2\cdot CO}{>}C:N\cdot OH$, has been studied as a more simple oximinoketone than violuric acid which contains nitrogen in the ring. The name dimethylviolanic acid is suggested for it. In addition to red and blue, it forms deep green alkali salts indicating that neither the third CO group nor the ring nitrogen in violuric acid are the cause of polychromism. The ring structure is, however, of importance, since oximinoacetylacetone, $(CH_3\cdot CO)_2C:N\cdot OH$, only forms orange to red salts and polychromic forms of the same salt do not exist. Moreover, these coloured salts are unstable. Ring structure alone does not cause polychromism, as neither fluorenoneoxime, benzo-phenoneoxime, benziloxime, nor oximinodibenzoylmethane exhibit the phenomenon.

When the cornflower-blue plates of sodium dimethylviolanate are

dissolved in methyl alcohol, the solution, likewise cornflower-blue, changes more or less quickly to bluish-green and then to a deep green, when the crystalline green chromoisomeride may be obtained from the solution. At the intermediate stage, it is possible to prepare crystal-line, bluish-green or greenish-blue mixed salts. All these solutions contain unimolecular partly dissociated salt, as proved by ebullioscopic measurements.

The green solution is characterised by a new second absorption band in the visible part of the spectrum, and belongs to a new series of chromoisomeric oximino-salts.

The change is rapid only in dilute solutions which are sufficiently dissociated, as it is retarded by additions which check the dissociation. The conductivity of the green isomeride is 2—3% less than that of the blue form.

The two forms differ chemically, the green form being very readily decomposed. In the case of oximinoacetylacetone the cæsium salt decomposes immediately, the rubidium salt can be kept for a time, and the potassium salt is relatively stable. The rate of decomposition, like the depth of colour, increases with the atomic weight of the metal.

Conductivity measurements indicate that dimethylviolanic acid contains yellow oxime ions, and has the structure

$$CMe_2 \!\! <^{CH_2 \cdot CO}_{CH_2 \cdot CO} \!\! > C{:}N \cdot OH,$$
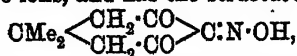
whereas the blue sodium salt is derived from a blue acid having a higher dissociation constant, and probably the nitrosoenol structure,

$$CMe_2 \!\! <^{CH_2 \cdot C(OH)}_{CH_2 {-}{-}CO} \!\! > C \cdot NO.$$ This result is in agreement with the optical behaviour.

The behaviour of the blue potassium salt and the red lithium salt of diphenylvioluric acid in methyl alcohol and in acetone indicates that the red lithium salt in acetone contains an internal alkali complex salt, whereas in the violet-red solution in methyl alcohol this complex has decomposed. Probably the yellowish-red and violet salts are not mixed salts, but their isomerism is not due to differences in partial valency. The copper-red magnesium dimethylviolanate forms a violet-red solution in water, and a red solution of very low conductivity in organic solvents.

The green sodium dimethylviolanate is considered to have the structure $CMe_2 \!\! <^{CH_2 {-}{-}CO}_{CH_2 \cdot C(ONa)} \!\! > C \cdot NO.$

Dimethylviolanic acid is prepared as described by Haas (T., 1906, 89, 189). The *methyl* ester forms a yellow, crystalline crust, m. p. 92°. The *magnesium* salt forms lustrous, bright copper-red platelets; the *copper* salt separates in brown platelets with a bronze lustre; the *silver* salt, $2H_2O$, forms a dark green, microcrystalline powder.

Phenylviolanic acid, $CHPh \!\! <^{CH_2 \cdot CO}_{CH_2 \cdot CO} \!\! > C{:}N \cdot OH$, is a pale yellowish-green, crystalline powder, m. p. 175°. When warmed with water a chocolate-brown, lustrous powder is obtained.

The alkali salts of oximinoacetylacetone are described.   E. F. A.

3-Methyl-1 : 2-diketohydrindene, an Analogue of Isatin.
JULIUS VON BRAUN and G. KIRSCHBAUM (*Ber.*, 1913, **46**, 3041—3050).
—*3-Methyl-*1 : 2 *diketohydrindene* is readily obtained by the action of
cold formaldehyde and hydrochloric acid on oximino-3-methyl-
hydrindone (compare Perkin, Roberts, and Robinson, T., 1912, **101**,
232). It strongly resembles isatin, having a deep reddish-yellow
colour, giving the same indophenine reaction, and dissolving in alkali
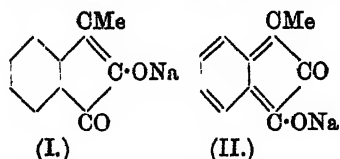
with a very intense bluish-violet
colour, which is much more stable
than the corresponding coloration
from isatin. Of the two possible
formulæ (I. and II.) for the sodium
salt, the authors are led to prefer (II),
since the great change in colour from
red to bluish-violet is better explained (especially in view of the fact that
the salts of 2-methyldiketohydrindene which must have a structure
similar to that of formula I, are red), whilst, also, the free diketone
gives no coloration with ferric chloride, and does not combine with
bromine, that is, it has no tendency towards enolisation of the usual
type. With benzoyl chloride, the sodium salt of 1 : 2-diketo-3-methyl-

hydrindene yields 1 : 2-*diketo-3-benzoyl-3-methylhydrin-
dene*, which is readily explained by 1 : 4-addition. In
this light, the authors are led to propose the annexed
formula for the bluish-violet salts of isatin prepared by
Heller (A., 1907, i, 442), and find confirmation, there-
fore, in the fact, that all derivatives of isatin, in which,
the carbonyl group adjacent to the NH group is substituted and
which themselves are red or brown, yield blue solutions with alkali,
whilst derivatives in which the β-carbonyl group is substituted yield
yellow or brown solutions with alkali.
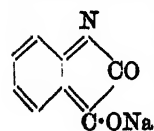
3-*Methyl-a-hydrindone*, b. p. 118—119°/11 mm., is obtained as a pale
yellow oil which could not be caused to solidfy by the action of
aluminium chloride on a solution of β-phenylbutyryl chloride in
light petroleum. The oily *phenylhydrazone, semicarbazone*, m. p.
230—231°, *oxime*, m. p. 141·5°, *benzylidene* derivative, m. p. 88—89°,
and *salicylidene* derivative, yellow needles, m. p. 172°, were analysed.
The regulated action of amyl nitrite and hydrochloric acid on an
alcoholic solution of 3-methyl-a-hydrindone leads to the formation of
the somewhat unstable oximinomethylhydrindone,

$$C_6H_4 \left< \begin{matrix} CHMe \\ CO \end{matrix} \right> C:N\cdot OH,$$
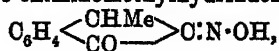
almost colourless crystals, m. p. 130°, which readily yields a *benzoyl*
derivative, m. p. 125°. Cold concentrated hydrochloric acid and
formaldehyde convert the oximino-derivative into 1 : 2-diketo-3-methyl-
hydrindene, which is obtained as a viscous red oil which could not be
distilled without decomposition and did not solidify. It yields

a *disemicarbazone*, m. p. 267° (decomp.),
and condenses with o-phenylenediamine in
warm methyl-alcoholic solution to a
quinoxaline derivative (annexed formula),
m. p. 202°. It dissolves instantly in
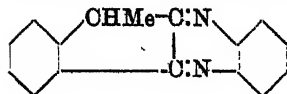
aqueous alkali with the formation of an intensely bluish-violet solution, which, in comparison with the similar solutions obtained from isatin or 1 : 2-diketohydrindene, is remarkably stable ; after four hours the colour commences to disappear, whilst after five hours the solution is dirty brown. Addition of acid then precipitates an *acid* which softens at 133°, and has m. p. 143° (decomp.). This substance could not be obtained pure, but probably has the composition

$$C_6H_4 \cdot Et \cdot CO \cdot CO_2H.$$
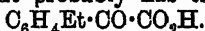
The rupture of the ring occurs more easily after benzoylation. When benzoyl chloride is added to an alkaline solution of the ketone, the *benzoyl* derivative, $C_{17}H_{12}O_3, H_2O$, m. p. 195° (decomp.), is precipitated, and the alkaline filtrate yields on acidification benzoic acid and a *diketo-acid*, $C_{17}H_{14}O_4$, m. p. 203°, which gives a *diphenylhydrazone*, $C_{29}H_{26}O_2N_4$, m. p. 238°, reaction occurring according to the scheme :

$$C_6H_4{<}^{CMe}_{C(ONa)}{>}CO \longrightarrow C_6H_4{<}^{CMeBz}_{CO}{>}CO \longrightarrow C_6H_4{<}^{CHMeBz}_{CO \cdot CO_2H}.$$
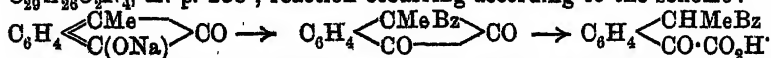
Methylhydrindone differs remarkably from hydrindone in its behaviour towards Grignard's reagents. Whereas the latter reacts vigorously with methyl magnesium iodide, yielding 1-*hydroxy*-1-*methylhydrindene*, $C_6H_4{<}^{CH_2}_{CMe(OH)}{>}CH_2$, b. p. 118°/14 mm., D_4^{20} 1·068, which can be distilled under ordinary pressure without notable elimination of water, the tertiary alcohol primarily formed from 3-methylhydrindone by a similar process loses the elements of water almost completely at 90°, and forms 1 : 3-*dimethylindene*,

$$C_6H_4{<}^{CHMe}_{CMe}{>}CH,$$
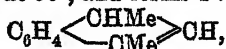
b. p. 212—214°/ordinary pressure, 86—88°/11 mm., D_4^{20} 0·9553, n_D^{20} 1·53444, which, unlike methylindene, is practically stable to air. It forms a *picrate*, yellow needles, m. p. 94—95°.   H. W.

1 : 2-Diketo-3-methylhydrindene. A Correction. Julius von Braun (*Ber.*, 1913, **46**, 3250. Compare preceding abstract).—The author has inadvertently overlooked the fact that the views advanced by him on the constitution of salts of isatin have been previously advocated by Ruhemann, T., 1909, **95**, 984).   H. W.

Diacetyldi-imino-α-naphthol and its Transformations. IV. Oswald Miller (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1480—1488. Compare this vol., i, 877).—Neither Meerson (A., 1888, 713) nor Kehrmann (A., 1895, i, 151) succeeded in obtaining diacetyldi-imino-α-naphthol by the action of acetic anhydride and sodium acetate on di-imino-α-naphthol hydrochloride. The latter, as the author has already pointed out (A., 1911, i, 308), crystallises with $2H_2O$, which partly decomposes the diacetyl compound at the moment of its formation ; the inaccuracy of Meerson's view that acetic anhydride plays a part in this decomposition, is evident from the fact that diacetyldi-imino-α-naphthol may be crystallised from this solvent, as from any other free from hydroxyl ions, without undergoing any decomposition.

Diacetyldi-imino-α-naphthol, $C_{14}H_{12}O_3N_2$, obtained by the action of

acetic anhydride and sodium acetate on anhydrous di-imino-α-naphthol hydrochloride, forms yellow prisms, m. p. 187°, and dissolves in fuming nitric acid or acetic acid with production in almost theoretical yields of acetylamino-1 : 4-naphthaquinone. The latter (1 mol.) combines with diacetyldi-iminonaphthol (1 mol.) to give the compound, $C_{14}H_{12}O_3N_2,C_{12}H_9O_8N$, m. p. 178° (decomp.), described by Meerson (*loc. cit.*). Decomposition of diacetyldi-iminonaphthol by heating in aqueous alcoholic solution results in the formation of four parts of 2-acetylamino-1 : 4-naphthaquinone and 1 part of 4-acetylamino-1 : 2-naphthaquinone.

The action of a glacial acetic acid solution of aniline on a solution of diacetyldi-iminonaphthol in 95% alcohol yields a mixture of the ordinary dianilide with a new anilide, 2-*acetylamino*-4-*phenylimino*-1 : 4-*naphthaquinone*, $C_{18}H_{14}O_2N_2$, which crystallises in yellowish-red needles, or in red plates with marked metallic lustre, m. p. 185°; by boiling acetic acid it is decomposed quantitatively into aniline and acetylamino-1 : 4-naphthaquinone. Its *platinichloride*,

$$(C_{18}H_{14}O_2N_2,HCl)_2,PtCl_4,$$
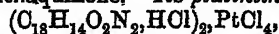
which forms yellowish-brown plates, is accompanied by that of 2-amino-4-phenylimino-1 : 4-naphthaquinone, m. p. 121° (compare Miller and Smirnov, A., 1911, i, 121). Thus, this new anilide, like the derivatives of naphthaquinones already investigated, shows a marked tendency to react in two directions.

The above method of obtaining the new anilide leads also to the formation of three compounds of this anilide with the dianilide : (1) $2C_{18}H_{14}O_2N_2,C_{22}H_{16}ON_2$, which forms reddish-yellow plates, m. p. 170—171°; (2) $1\cdot66C_{18}H_{14}O_2N_2,C_{22}H_{16}ON_2$, which forms red plates, m. p. 147—148°; (3) red needles and plates, m. p. 160°. The melting points of these compounds rise on melting and re-solidification.

<div align="right">T. H. P.</div>

The Three Isomeric Di-α-naphthoylbenzenes. CHRISTIAN SEER and OTTO DISCHENDORFER (*Monatsh.*, 1913, **34**, 1493—1502).—The *p*- and *m*-di-α-naphthoylbenzenes have been prepared by condensing terephthalyl chloride and *iso*phthalyl chloride respectively, with naphthalene in cold carbon disulphide solution, by means of aluminium chloride. Since phthalyl chloride reacts in the unsymmetrical form, and α-naphthoyl-*o*-benzoyl chloride will not react in the cold, such a condensation could not be carried out for the ortho-isomeride. The latter was obtained, however, from α-naphthoyl-*o*-benzoic acid by Guyot and Vallette's method (A., 1911, i, 652).

The yield of crude, light brown p-*di-α-naphthoylbenzene*,

$$C_6H_4(CO\cdot C_{10}H_7)_2,$$
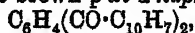
was very high, but the compound was obtained crystalline with great difficulty, by distilling the crude product, dissolving the oily distillate, b. p. 315—330°/11—20 mm., in boiling glacial acetic acid, and filtering from resinous matter as soon as crystals appeared. It forms, colourless, glistening leaflets, m. p. 233—234°, and gives a blood-red solution in sulphuric acid. m-*Di-α-naphthoylbenzene* was also obtained in good yield in colourless, glistening leaflets from dilute pyridine, m. p. 191°.

α-Naphthoyl-*o*-benzoic acid was reduced by zinc and 80% acetic acid,

when the *lactone* of *phenyl-α-naphthylcarbinol-o-carboxylic acid*,

$$C_{10}H_7 \cdot CH \underset{C_6H_4}{\overset{O}{<}} CO,$$
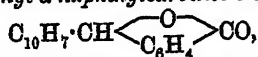
crystallised on cooling. It was purified by extraction with boiling dilute hydrochloric acid, and formed faintly yellow spikelets from alcohol, m. p. 135—136°. The lactone was treated with magnesium α-naphthyl bromide, and the white, flocculent magnesium compound was decomposed with dilute hydrochloric acid, when 2 : 5-*di-α-naphthyl*-3 : 4-*benzofuran*, $C_6H_4 \underset{C(C_{10}H_7)}{\overset{C(C_{10}H_7)}{<}} O$, was obtained in bright yellow, glistening needles, m. p. 166°, which give deep yellow solutions with brilliant green fluorescence. On oxidation with sodium dichromate and acetic acid, a quantitative yield of o-*di-α-naphthoylbenzene* was obtained. This isomeride is freely soluble, forms colourless needles, m. p. 130—131°, and condenses with hydrazine hydrate to 1 : 4-*di-α-naphthylphthalazine*, $C_6H_4 \underset{C(C_{10}H_7):N}{\overset{C(C_{10}H_7):N}{<}}$, which crystallises in rhombic plates, m. p. 176°.

Attempts to prepare condensation products by heating these isomeric diketones with aluminium chloride were without success.

J C W.

Preparation of Bromoaminoanthraquinones. BADISCHE ANILIN- & SODA FABRIK (D.R.-P. 263395, 265727. Compare this vol., i, 1071).—The preparation of 3-bromo-2-aminoanthraquinone from 1-bromo-2-aminoanthraquinone-3-sulphonic acid by elimination of the sulphonic group (with sulphuric acid) and migration of the bromine atom has been previously described; and it is now found that this reaction is a general one when a bromine atom, amino- and sulphonyl group are all present in the same benzene nucleus.

3 : 7-Dibromo-2 : 6-diaminoanthraquinone is prepared by heating sodium 1 : 5-dibromo-2 : 6-diamino-3 : 7-disulphonate with 20 parts of sulphuric acid (60° Bé.) at 180—190°; it does not react with aniline.

3 : 6-*Dibromo-2 : 7-diaminoanthraquinone* is obtained in a similar manner from 1 : 8-dibromo-2 : 7-diaminoanthraquinone-3 : 6-disulphonic acid, and does not react with aniline or p-toluidine.

4-*Bromo*-1-*aminoanthraquinone*-2-*sulphonic acid* is obtained by sulphonating, and subsequently brominating (in aqueous solution), 1-aminoanthraquinone; when it is boiled with concentrated sulphuric acid it gives rise to 2-bromo-1-aminoanthraquinone (*loc. cit.*).

The second patent states that if the heating in the reactions described previously is carried out for a few moments only in the presence of mercury (or its salts) that the sulphonic group is eliminated, but the migration of the bromine atom does not occur; thus, when sodium 1-bromo-2-aminoanthraquinone-3-sulphonate (10 parts) is heated with 100 parts of sulphuric acid (66° Bé.) and mercury sulphate (0·5 part) at 180° during three minutes, it gives rise to 1-bromo-2-aminoanthraquinone, which readily furnishes 2-*amino*-1-p-*toluidinoanthraquinone* with p-toluidine, whilst 4-bromo-1-aminoanthraquinone-2-sulphonic acid gives rise to 4-bromo-1-aminoanthraquinone.

F. M. G. M.

Bromohydroxynaphthaquinones. V. OSWALD MILLER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1467—1479).—The author finds that the dibromide, m. p. 149·5—151·5°, described by Diehl and Merz (*Ber.*, 1881, **14**, 1912) does not exist, and establishes the identity of the bromohydroxynaphthaquinones prepared from : (1) the dibromide, m. p. 218° (compare Miller, A., 1885, 667); (2) 2-hydroxy-α-naphthaquinone (compare Diehl and Merz, A., 1878, 888); (3) α-naphthaquinoneanilide (compare Balzer, A., 1882,204), and (4) bromo-β-naphthaquinone (compare Zincke, A., 1887, 53). In the last of these methods, which is aerobic, only one-third of the oxygen absorbed reacts according to the equation $C_{10}H_{15}O_2Br + O = C_{10}H_5O_3Br$, the remaining two-thirds acting on a second molecule of the bromonaphthaquinone to form secondary products.

3-*Bromo-2-hydroxy-1 : 4-naphthaquinone*, $C_6H_4 <^{CO \cdot C(OH)}_{CO \cdot CBr}$, crystallises in monoclinic prisms or hemihedral forms, m. p. 198·5° (corr. 202°). The canary-yellow colour of the powdered compounds persists on heating to 170°, at which temperature a number of orange-yellow spots make their appearance. These spots gradually increase in magnitude as the temperature is raised, until at 190° the whole mass exhibits the orange-yellow colour, the powder becoming converted at the same time into small prisms. On cooling, these prisms become somewhat paler and undergo disintegration. The golden-yellow liquid obtained on fusion solidifies only at about 170°, but subsequently melts as before at 198·5°. The identity of the products yielded by the different methods of preparation was ascertained by investigation of (1) the solubility in 95% alcohol; (2) the potassium salt, which is anhydrous; (3) the barium salt ($+4H_2O$), and (4) the aniline salt, m. p. 166·5° (decomp.). The homogeneity of the compound was established by heating it at various temperatures for ten hours, the non-volatilised residues in all cases melting at 198·5°.

The yields of phthalic acid obtained by oxidising various naphthaquinone derivatives by means of potassium permanganate in sulphuric acid solution are: α-naphthaquinone, 95·2%; 2-hydroxy-α-naphthaquinone, 93·4%; bromohydroxynaphthaquinone from Miller's dibromide, m. p. 218°, 96·4%; bromohydroxynaphthaquinone from 2-hydroxy-α-naphthaquinone, 97·3%. These results are regarded as a confirmation of the ordinary structural formula for naphthalene.

T. H. P.

Purpurogallin. I. MAXIMILIAN NIERENSTEIN and C. W. SPIERS (*Ber.*, 1913, **46**, 3151—3157).—The authors have oxidised pyrogallol by several processes, and have shown that the purpurogallin obtained is identical in all cases. This substance has the formula $C_{11}H_8O_5$, contains four free hydroxyl groups (estimated by Zerevitinov's method, A., 1908, i, 593, in a modified apparatus) and a carbonyl group, and yields naphthalene on distillation with zinc dust. The oxidation was effected by the following means: with sodium nitrite and acetic acid (Perkin and Steven, T., 1903, **83**, 197), which is the best method, and yields 10—16% of the substance; with silver nitrate or acid permanganate (Girard, 1869); with chromic acid or *p*-benzoquinone

(Wichelhaus, A., 1872, 172, who called the compound, in the latter case, pyrogalloquinone, and obtained quinol as a by-product) ; by passing a current of air through a solution of pyrogallol and gum arabic (Struve, A., 1872, 703) ; with horse-radish peroxydase ; with potassium ferricyanide (Hooker, A., 1888, 292), and by electrolysis (Perkin and Perkin, T., 1904, **85**, 243).

Purpurogallin was obtained in deep-red needles from glacial acetic acid. It always melted at 274—275° in a sulphuric acid bath, but in a paraffin bath, or in very long capillary tubes, it sublimed without melting.

Tetra-acetylpurpurogallin was easily prepared in orange-yellow needles, m. p. 179—180° (Herzig, A., 1910, i, 677, described a colourless product). The molecular-weight determinations with certain solvents gave abnormal results, which could be explained in the case of acetic acid by partial hydrolysis to *monoacetylpurpurogallin*, which formed brownish-red needles, m. p. 169—170°; these could be separated mechanically. The tetra-acetyl derivative was completely hydrolysed by 50% acetic acid, and readily formed a *phenylhydrazone*, $C_{11}H_4O_4(COMe)_4{:}N{\cdot}NHPh$, in brick-red needles, m. p. 254—258°.

The authors are studying the formation of hydroxy-*o*-benzoquinone, which Wichelhaus, Perkin and Steven, and Perkin (T., 1913, **104**, 661) have assumed to represent an intermediate stage in the oxidation of pyrogallol.   J. C. W.

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 265725).—When aminoanthraquinones are heated at 200—220° with naphthols in the presence of zinc chloride they furnish condensation products which are formed from 1 molecule of the aminoanthraquinone and 2 molecules of the naphthol, with elimination of 3 molecules of water. The following *compounds* are described : (1) from 1-aminoanthraquinone with β-naphthol, a red, crystalline powder ; (2) from 2-aminoanthraquinone with β-naphthol, a yellowish red, crystalline powder ; (3) from 1-aminoanthraquinone with α-naphthol, a dark violet powder, and (4) from 4-chloro-1-aminoanthraquinone with β-naphthol, a red, crystalline powder.   F. M. G. M.

Retene. III. Condensation of Retenequinone with Ketonic Compounds. ALFRED HEIDUSCHKA and CH. KHUDADAD (*Arch. Pharm.*, 1913, **251**, 401—437. Compare A., 1912, i, 107).—Retenequinone, which resembles benzil and phenanthraquinone in its behaviour towards organomagnesium haloids (Heiduschka and Grimm, *loc. cit.*), has been examined as to its behaviour during condensation with various types of ketones, to ascertain whether its analogy to benzil and phenanthraquinone is also evident in such reactions. In the presence of aqueous or, better, alcoholic potassium hydroxide, retenequinone (1 mol.) condenses with only 1 mol. of an aliphatic ketone, $CH_2R{\cdot}COMe$ (where R may be hydrogen and no negative group, other than the carbonyl, is present) to form, unlike benzil and phenanthraquinone, only one product. Four formulæ are possible for the substance, but the two containing $>C{:}CR{\cdot}$ are excluded because the condensation product is rapidly attacked by Baeyer's reagent, whereby the presence

of the group $>$C:CH· is indicated. The condensation product, therefore, may have the constitution : $C_{16}H_{16}<\genfrac{}{}{0pt}{}{C:CH\cdot CO\cdot CH_2R}{CO}$ or

$$C_{16}C_{16}<\genfrac{}{}{0pt}{}{C=\!=\!=CH}{C(OH)\cdot CHR}>CO\ ;$$
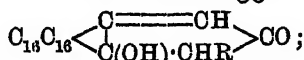
the first, however, is excluded because the substance, except where R is hydrogen, does not condense with benzaldehyde in alkaline solution, thereby showing that a methyl or methylene group adjacent to a carbonyl group is not present.

Anhydroacetoneretenequinone, $C_{16}H_{16}<\genfrac{}{}{0pt}{}{C=\!=\!=CH}{C(OH)\cdot CH_2}>CO$, m. p. 206·5°,

colourless needles, does not react with phenylhydrazine or with phenylcarbimide in the cold, condenses with benzaldehyde in the presence of alcoholic potassium hydroxide to form a *substance*, $C_{23}H_{24}O_2$, m. p. 203—204° (decomp.), pale yellow needles, and is reduced by zinc dust and acetic acid to a *substance*, $C_{21}H_{20}O$, m. p. 201°, colourless needles. *Methylanhydroacetoneretenequinone*,

$$C_{16}H_{16}<\genfrac{}{}{0pt}{}{C=\!=\!=CH}{C(OH)\cdot CHMe}>CO,$$
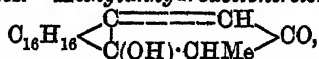
m. p. 205°, colourless needles, obtained together with a small quantity of an isomeride from methyl ethyl ketone, forms a *dibromide*, $C_{22}H_{22}O_2Br_2$, m. p. about 195° (decomp.), and is reduced to a *substance*,

probably $C_{16}H_{16}<\genfrac{}{}{0pt}{}{C-\!-CH_2}{C\cdot CHMe}>CO$, m. p. 153—155°, by zinc dust and

acetic acid, or by boiling hydriodic acid, D 1·96, and to a *substance*, $C_{22}H_{24}O$, m. p. 192—193° (decomp.), by zinc and alcoholic hydrochloric acid. Retenequinone and methyl propyl ketone yield *ethylanhydroacetoneretenequinone*, $C_{23}H_{24}O_2$, m. p. 186—187°, colourless needles. Retenequinone condenses with methyl hexyl ketone and with methyl hexenyl ketone to form corresponding *substances*, $C_{26}H_{30}O_2$, m. p. 181—182°, and $C_{26}H_{28}O_2$, m. p. 213—214°, both colourless needles, and with mesityl oxide (only in the presence of alcoholic potassium hydroxide) to form iso*propylideneanhydroacetoneretenequinone*, $C_{24}H_{24}O_2$, m. p. 219°.

Retenequinone and benzyl methyl ketone in the presence of aqueous potassium hydroxide yield two *substances*, one, probably

$$C_{16}H_{16}<\genfrac{}{}{0pt}{}{C:CPh\cdot COMe}{C:CPh\cdot COMe}'$$
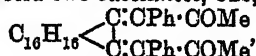
m. p. 200—202° (decomp.), faintly red crystals, the other, $C_{45}H_{40}O_2$, m. p. 214—215°, deep red crystals ; the residue from the mother liquor, by boiling with glacial acetic acid, yields a *substance*, $C_{29}H_{26}O_3$, m. p. 210—212°, colourless needles, which is *phenylanhydroacetoneretenequinone acetate*, since it is also obtained by heating phenylacetoneretenequinone with glacial acetic acid. *Phenylacetoneretenequinone*,

probably $C_{16}H_{16}<\genfrac{}{}{0pt}{}{C(OH)\cdot CHPh\cdot COMe}{CO}$, m. p. 190—192° (decomp.),

yellow crystals, is obtained from retenequinone and benzyl methyl ketone in the presence of alcoholic potassium hydroxide.

Retenequinone and ethyl acetonedicarboxylate in the presence of

alcoholic potassium hydroxide condense to form a *substance*, $C_{27}H_{28}O_6$, m. p. 185—187° (decomp.), yellow needles or leaflets, which receives the constitution $C_{16}H_{16}$<$\begin{smallmatrix} C ==== C(CO_2Et) \\ | \\ C(OH)\cdot CH(CO_2Et) \end{smallmatrix}$>$CO$.

Retenequinone and ethyl benzoylacetate, by treatment with acetic anhydride and a little concentrated sulphuric acid at 45—50° yield a *substance*, $C_{40}H_{36}O_6$, m. p. 235°, faintly yellow needles, which is probably $C_{16}H_{16}$<$\begin{smallmatrix} C:CBz\cdot CO_2Et \\ | \\ C:CBz\cdot CO_2Et \end{smallmatrix}$>.   C. S.

Action of Zinc on a Mixture of Fenchone and Allyl Iodide. MICHAEL ZAJCEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1578—1580).—The action of zinc on a mixture of fenchone and allyl iodide in presence of ether yields *allylfenchyl*, $C_{13}H_{22}O$, b. p. 107—109°, D_0^0 0·9747, D_{20}^{20} 0·96144, D_4^{20} 0·9597, $[\alpha]_D$ +12·44°, n_D 1·49143. Attempts to prepare the corresponding *chloride*, $C_{13}H_{21}Cl$, by saturating allylfenchyl with dry hydrogen chloride in the cold, yielded an impure product, b. p. 122—124°. The investigation is being continued.   T. H. P.

Synthesis of 3-Ethylpulegol. MICHAEL ZAJCEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1571—1577).—The preparation of 3-methylpulegol by the action of magnesium and methyl bromide on pulegone was unsuccessfully attempted by Grignard (A., 1901, i, 679) and by Rupe and Emmerich (A., 1908, i, 556), and this compound has only recently been prepared (compare Rupe, Schobel and Abegg, A., 1912, i, 573). The corresponding ethyl compound is, however, readily obtainable.

3 - *Ethylpulegol*, $CHMe$<$\begin{smallmatrix} CH_2\cdot CEt(OH) \\ CH_2 —— CH_2 \end{smallmatrix}$>$C:CMe_2$, has b. p. 105—110°/9 mm., D_0^0 0·9379, D_{20}^{20} 0·9239, D_4^{20} 0·9223, $[\alpha]_D^{20}$ +43·22°, and exhibits normal cryoscopic behaviour in benzene. When oxidised by means of permanganate, it yields (1) the *trihydric alcohol*,

$$CHMe<\begin{smallmatrix} CH_2\cdot CEt(OH) \\ CH_2 —— CH_2 \end{smallmatrix}>C(OH)\cdot CMe_2\cdot OH,$$
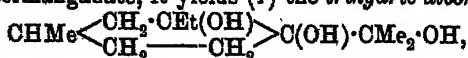
which is a viscous, cinnamon-coloured liquid; (2) β-methyladipic acid; (3) formic acid, and other products.   T. H. P.

Chemistry of Caoutchouc. VII. Theory of Vulcanisation. V. DAVID SPENCE and J. YOUNG (*Kolloid. Zeitsch.*, 1913, **13**, 265—271. Compare A., 1912, i, 706).—Further experiments have shown that there is no lower limiting temperature, as previously suggested, below which vulcanisation does not take place. By extending the period of observation it has been found that vulcanisation occurs at 50°, and from experiments made at intervals of 5° between 50° and 75°, the velocity of the vulcanisation process increases on the average in the ratio of 2·84:1 for a rise of temperature of 10°. The value of the temperature-coefficient lends support to the view that the vulcanisation process is a chemical change.

From comparative experiments on the speed of the vulcanisation

...

of caoutchouc, gutta-percha, and balata at 135°, it appears that the rate of the change is practically the same in all three cases. In each case, also, the vulcanisation reaches a limit when the quantity of sulphur, non-extractable with acetone, amounts to 32%. This proportion of sulphur corresponds with the formula $(C_{10}H_{16}S_2)_n$, and it is supposed that this compound is formed from each of the three substances.

The difference between caoutchouc, gutta-percha, and balata is considered to have its origin in differences in the colloidal condition of the hydrocarbon, the close similarity in the behaviour on vulcanisation being entirely opposed to the view that the differences are chemical in nature. H. M. D.

Formation of the Anthocyan Pigments of Plants. VI. FREDERICK KEEBLE, E. FRANKLAND ARMSTRONG, and W. NEILSON JONES (*Proc. Roy. Soc.*, 1913, B, 87, 113—131. Compare A., 1912, ii, 673 ; this vol., i, 325, 803).—The pale yellow sap colour of the petals of the wallflower is a mixture of hydroxyflavone glucosides (compare A. G. Perkin, T., 1896, 1566 ; Perkin and Pilgrim, T., 1898, 267). The mixture is hydrolysed by heating with acids and more slowly by emulsin. The hydrolysed pigment if reduced and subsequently oxidised yields a red pigment. A red pigment is obtained from most flowers containing similar soluble yellow pigments, suggesting that red mutations should be of possible occurrence in such species.

Oxidation by oxydase of the hydrolysed products of glucosides in presence of amino-acids yields pigments. Arbutin, for example, yields a red pigment probably produced by the interaction of quinhydrone with ammonia. It is suggested that many of the pigments and odorous substances formed during the ripening of fruits arise as results of reactions of this type.

A competition for oxydase ensues when a mixture of phenols is treated with a plant oxydase.

Quinol monomethyl ether gives no colour reaction with oxydase, but when a little benzidine solution is added, a deep and persistent carmine colour is obtained. The benzidine acts catalytically, playing the part of an organic peroxide, and bringing about the oxidation of a substance which resists the action of oxydase and hydrogen peroxide. It is suggested that the higher members of a flower colour series owe their origin to the presence of specific substances which, acting as receivers of oxygen, reduce the pigments characteristic of the lower members of the colour series, accept oxygen therefrom, and become oxidised to pigments of specific colour. E. F. A.

Anthocyanins. I. Pigment of Cornflowers. RICHARD WILLSTÄTTER and ARTHUR E. EVEREST (*Annalen*, 1913, 401, 189—232).—Since Morot in 1849, and Frémy and Cloëz in 1854, isolated in an impure state the blue pigment of the cornflower, very little work has been recorded, probably on account of the instability of the anthocyanin. An important observation by Molisch (*Bot. Zeit.*, 1905, 63, 145), that in the flowers and red leaves of many plants the anthocyanin occurs, not merely in solution in the cell juice, but also in the crystal-

line or amorphous state, revived interest in the subject, and observations, many of which are erroneous, have been recorded by Grafe, by Glan, by Griffiths (A., 1904, i, 179), and by Combes (A., 1911, ii, 1125).

Anthocyanins are the blue, violet, and red pigments which are extracted from flowers, fruits, and many leaves by water or aqueous alcohol, and are insoluble in ether; they are roughly classified by their colour reactions in acid and in alkaline solution and with lead acetate. For the sake of completeness, it may be recalled that red and blue flowers also contain yellow pigments, anthoxanthins, which are soluble in water or dilute alcohol, and are quite different from the chemically indifferent carotins. The blue pigment of the cornflower is unstable and very difficult to isolate, and has not yet been obtained crystalline. The various shades of colour in different parts of the flower are due to various derivatives of one substance. Thus the blue pigment is the potassium salt of an acid (cyanin), the violet pigment is the free acid, and the red pigments are oxonium salts of cyanin and plant-acids. In addition, a colourless substance can be isolated from the flowers, which is an isomeride of cyanin and is acid and forms colourless alkali salts.

All anthocyanins are present in flowers as glucosides and not, as previously stated by Grafe, partly in combination with dextrose and partly not. They all exhibit a characteristic reaction, the anthocyanidin reaction; an anthocyanin dissolved in N- or $2N$-sulphuric acid is quite unaffected by shaking with amyl alcohol, but after hydrolysis on the water-bath, the coloured fission product (anthocyanidin) is quantitatively extracted by the alcohol, forming a reddish-violet solution, which is changed to bluish-violet by washing, or more rapidly by sodium acetate. (In this connexion, Erdmann's test for new, or comparatively new, red wine is discussed.)

In order to isolate the colouring matter, dried cornflower meal, mixed with six parts of sand to facilitate filtration, is rapidly extracted with water or 20% alcohol, preferably in the presence of sodium nitrate or chloride to retard the change of the anthocyanin to the colourless modification. The deep blue solution is treated with alcohol and the potassium cyanin, after repeated fractional precipitation with water and alcohol, is obtained mixed with at least twice the weight of carbohydrates, albumins, and pentosans. In its further purification, the blue pigment is treated with alcohol and hydrochloric acid, whereby the pentosans (one of which is probably xylan) are precipitated, and the pigment is converted in *cyanin chloride*, $C_{28}H_{33}O_{17}Cl,3H_2O$, m. p. 203—204° (corr.) (anhydrous), dark blue, rhombic leaflets with golden reflex. The chloride is extremely hygroscopic, and forms stable red solutions in acids; its aqueous solution rapidly becomes colourless, but recovers its red colour by the addition of an acid. A solution of the chloride becomes violet in the presence of calcium carbonate, and changes from red through violet to cornflower blue by treatment with sodium carbonate.

By hydrolysis with boiling 20% hydrochloric acid for three to three and a half-minutes, cyanin chloride yields dextrose (2 mols.) and *cyanidin chloride*, $C_{16}H_{13}O_7Cl$, long, brownish-red, metallic needles,

which decomposes by slow heating, but has m. p. 220° (decomp.) when placed directly in a bath at this temperature. Like cyanin chloride, cyanidin chloride is converted by aqueous sodium carbonate, firstly, into a violet solution of the acid, cyanidin, and then into a blue solution of sodium cyanidin. Moreover, cyanidin chloride in dilute alcohol at 85° is slowly converted into an *isomeride*, colourless crystals, which is reconverted into red cyanidin salts by boiling dilute mineral acids; by prolonged keeping of its aqueous alcoholic or ethereal solution, the colourless isomeride changes to another *substance*, colourless needles, from which the red cyanidin salts cannot be regenerated.

Little can be stated at present with regard to the constitutions of cyanin and cyanidin. The fact, that the two substances form very stable salts with hydrochloric acid, indicates that cyanin and cyanidin are related to benzopyronium (Decker and Fellenberg, A., 1909, i, 116) rather than to the flavones. C. S.

Hydrogenation of a Secondary Alcohol derived from Furfuraldehyde in the Presence of Nickel. ROGER DOURIS (*Compt. rend.*, 1913, **157**, 722—724).—During the catalytic hydrogenation of certain secondary α-ethylenic alcohols, dehydration occurs, followed by hydrogenation of the ethylenic hydrocarbon produced. The author is extending this study to heterocyclic alcohols derived from furfuraldehyde. Furfuraldehyde itself gives α-methylfuran, α-methyltetrahydrofuran, methyl propyl ketone, and pentan-β-ol (compare Padoa and Ponti, A., 1907, i, 146). Furylethylcarbinol on hydrogenation in the presence of reduced nickel at 175° yields propyltetrahydrofuran, dipropyl ketone, *ethyltetrahydrofurylcarbinol*, $C_4H_7O\cdot CHEt\cdot OH$, a colourless, syrupy liquid, b. p. 87—90°/15 mm., D_4^0 1·0051, D_4^{20} 0·9869, and a small quantity of a liquid, b. p. 110—120°/15 mm., which contains a glycol.

Whilst furylethylcarbinol, unlike its propyl and *iso*amyl homologues, will not yield an acetic ester, yet its tetrahydro-derivative readily yields an *ester*, a colourless liquid, b. p. 90—91°/12 mm., D_4^0 1·0334, D_4^{16} 1·0149. W. G.

Action of Fermenting Yeast on Furfuraldehyde. Formation of Furyltrimethylene Glycol. II. CARL J. LINTNER and H. J. VON LIEBIG (*Zeitsch. physiol. Chem.*, 1913, **88**, 109—121. Compare A., 1911, ii, 816).—Furfuraldehyde in presence of yeast which is actively fermenting sucrose is converted into *furyltrimethylene glycol* [$\alpha\gamma$-dihydroxy-α-furylpropane], $C_4H_3O\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot OH$. This crystallises in very tiny needles, m. p. 50·5°, $[\alpha]_D$ – 10·5°; with concentrated sulphuric acid it gives a gentian-blue coloration.

The *diacetate* forms a pale yellow oil with an aromatic odour, b. p. 246—248°/720 mm.; the *dibenzoyl* derivative is likewise a pale yellow oil. Both compounds have a normal molecular weight and give a blue coloration with sulphuric acid.

The *di-p-nitrobenzoate* forms an almost colourless, crystalline powder, m. p. 150—151°. The *diphenylurethane*, which is a colourless, light powder, has m. p. 195°.

It is assumed that the acetaldehyde formed as the first product of the fermentation of dextrose undergoes an aldol condensation with furfuraldehyde and that this aldol is immediately reduced to the glycol by the yeast.   E. F. A.

Thioflavones [2-Phenyl-1 : 4-benzothiopyrones]. SIEGFRIED RUHEMANN (*Ber.*, 1913, 46, 3384—3395).—The sodium salts of the thiophenols, like the ordinary phenols (this vol., i, 891), can undergo condensation with ethyl phenylpropiolate with formation of the ethyl esters of the corresponding β-arylthiolcinnamic acids. The free acids on heating lose carbon dioxide with formation of arylthiolstyrenes, and by successive treatment with phosphorus pentachloride and aluminium chloride they are almost quantitatively converted into thioflavones (2-phenyl-1 : 4-benzothiopyrones). The last-named substances are more resistant than the flavones towards alkali, but by prolonged boiling with concentrated potassium hydroxide solution two concurrent decompositions are effected, one yielding (with thioflavone itself) benzoic acid and o-thiolacetophenone, and the other acetophenone and o-thiolbenzoic acid.

The corresponding 1 : 4-benzothiopyrone, $C_6H_4{<}^{CO \cdot CH}_{S-CH}$, could not be produced in a similar manner on account of the impossibility of hydrolysing ethyl phenylthiofumarate (obtainable from the sodium compound of the thiophenol and ethyl chlorofumarate) without complete decomposition.

Ethyl β-o-tolylthiolcinnamate, $C_6H_4Me \cdot S \cdot CPh{:}CH \cdot CO_2Et$, a viscous, yellow oil, b. p. 230°/12 mm., which slowly crystallises, is obtainable by the gradual addition of ethyl phenylpropiolate to a hot solution of sodium in excess of o-tolyl mercaptan diluted with toluene ; *β-o-tolylthiolcinnamic acid*, produced by hydrolysis with alcoholic potassium hydroxide, forms colourless needles, m. p. 160—161° (decomp.), and on heating passes into o-*tolylthiolstyrene*, $C_6H_4Me \cdot S \cdot CPh{:}CH_2$, a yellow oil, b. p. 183—184°/12 mm., with loss of carbon dioxide. When powdered aluminium chloride is gradually introduced into a mixture of phosphorus pentachloride and β-o-tolylthiolcinnamic acid in benzene, intramolecular condensation to 2-*phenyl-8-methyl-1* : 4-*benzothiopyrone* (8-*methylthioflavone*), $C_6H_3Me{<}^{CO \cdot CH}_{S-CPh}$, pale yellow needles, m. p. 124—125°, is effected.

p-Tolyl mercaptan, obtained by reduction of *p*-toluenesulphonyl chloride, condenses in a similar manner to the ortho-isomeride, with ethyl phenylpropiolate, producing the *ethyl* ester, yellowish prisms, m. p. 77—78°, b. p. 240—242°/12 mm., of β-*p*-tolylthiolcinnamic acid, colourless needles, m. p. 167° (decomp.). By successive treatment with phosphorus pentachloride and aluminium chloride the acid is converted into 2-*phenyl-6-methyl-1* : 4-*benzothiopyrone* (6-*methylthioflavone*), colourless needles, m. p. 153—154°.

Thiol-*p*-xylene, b. p. 211—212°, obtained from the corresponding sulphinic acid, which was prepared by the diazo-reaction, condensed with ethyl phenylpropiolate, giving the viscous, yellow *ethyl* ester,

b. p. 242°/12 mm., of *β-p-xylylthiolcinnamic acid*, colourless prisms, m. p. 186—187° (decomp.). Treatment with phosphoric and aluminium chlorides converts this into 2-*phenyl*-5 : 8-*dimethyl*-1 : 4-*benzothiopyrone* (5 : 8-*dimethylthioflavone*), $C_6H_2Me_2 \begin{subarray}{l} \text{CO·CH} \\ \diagdown\text{S——CPh} \end{subarray}$, colourless needles, m. p. 133—134°.

Thiol-*m*-xylene, b. p. 212—214°, in a similar manner, condenses with ethyl phenylpropiolate, giving the *ethyl* ester, yellow prisms, m. p. 91—92°, b. p. 242—244°/12 mm., of *β-m-xylylthiolcinnamic acid*, yellow prisms, m. p. 184° (decomp.). This acid, when heated, loses carbon dioxide with formation of 3 : 4-*dimethylphenylthiolstyrene*, a yellow oil, b. p. 197—198°/14 mm., and under the usual treatment with phosphoric and aluminium chlorides gives rise to 2-*phenyl*-6 : 8-*dimethyl*-1 : 4-*benzothiopyrone* (6 : 8-*dimethylthioflavone*), yellow needles, m. p. 152—153°.

o-Anisyl mercaptan, in the form of its sodium compound, reacts with ethyl phenylpropiolate in the general manner, giving the *ethyl* ester, colourless needles, m. p. 67—68°, b. p. 246—248°/12 mm., of *β-o-anisylthiolcinnamic acid*, colourless needles, m. p. 148° (decomp.). The acid is readily converted into 8-*methoxy*-2-*phenyl*-1 : 4-*benzothiopyrone* (8-*methoxythioflavone*), $OMe·C_6H_3 \begin{subarray}{l} \text{CO·CH} \\ \diagdown\text{S——CPh} \end{subarray}$, colourless needles, m. p. 129—130°. This compound, like the oxygen analogue (*loc. cit.*), can be demethylated by hydriodic acid, producing 8-*hydroxy*-2-*phenyl*-1 : 4-*benzothiopyrone*, yellow prisms, m. p. 292° (decomp.).

The sodium compound of *p*-anisylmercaptan with ethyl phenylpropiolate produces the *ethyl* ester, b. p. 255—256°/14 mm., of *β-p-anisylthiolcinnamic acid*, colourless prisms, m. p. 217—218° (decomp.). This was transformed in the usual manner into 6-*methoxy*-2-*phenyl*-1 : 4-*benzothiopyrone* (6-*methoxythioflavone*), colourless needles, m. p. 155—156°.

The behaviour of the benzothiopyrone compounds with alkali, towards which they are very stable, was especially investigated with 2-phenyl-1 : 4-benzothiopyrone (that is, thioflavone itself). It is completely changed by boiling with concentrated alcoholic sodium hydroxide for five to six hours; acetophenone, *o*-thiolacetophenone, as an oil oxidisable to dithiodiacetophenone $(C_6H_4Ac)_2S_2$, needles, m. p. 167—168° (compare Farbwerke Meister, Lucius, & Brüning, A., 1908, i, 987), benzoic acid, *o*-thiolbenzoic acid, and dithiodisalicylic acid could be recognised among the reaction products. D. F. T.

Aconitine Alkaloids. Pyraconitine. HEINRICH SCHULZE and A. LIEBNER (*Arch. Pharm.*, 1913, **251**, 453—467. Compare Schulze and Bierling, this vol., i, 287).—Pyraconitine, $C_{32}H_{43(or 41)}O_9N$ (Dunstan and Carr give $C_{31}H_{41}O_{10}N$; T., 1894, **65**, 176), prepared by heating aconitine at 192°, has m. p. 171°, $[\alpha]_D^{20}$ − 112·2°, in 95% alcohol ($c = 8·6918$), and crystallises from ether in colourless needles containing $1\frac{1}{2}Et_2O$, and from alcohol in crystals containing $2\frac{1}{2}EtOH$. Dunstan and Read's pyrojapaconitin (T., 1900, **77**, 60), obtained by heating japaconitine at 192°, is identical with pyraconitine. The following

salts, prepared in all cases from both pyraconitine and "pyrojap-aconitine," are described : hydrochloride, m. p. 167° (decomp.); auri-chloride, m. p. 157—158° (decomp.) ; hydrobromide, m. p. 240—242° (decomp.) (hydrated) or 243—244° (decomp.)(anhydrous), $[a]_D^{20} - 105\cdot87°$ in water ($c = 4\cdot5339$); hydriodide, m. p. 157—158° (decomp.) (hydrated), and perchlorate, m. p. about 190°. The preceding constants differ from those recorded by Dunstan and Carr (*loc. cit.*).   C. S.

*iso*apoCaffeine. HEINRICH BILTZ [with PAUL KREBS and KARL STRUFE] (*Ber.*, 1913, **46**, 3407—3410).—The substance *iso*apocaffeine, which is obtained together with *apo*caffeine in the oxidation of caffeine and 1 : 3 : 7-trimethyluric acid (Biltz and Krebs, A., 1910, i, 523), is 3 : 7-dimethylcaffolide ; this has been demonstrated by a course of degradation detailed in this paper. The formation of *iso*apocaffeine from caffeine or trimethyluric acid must evidently be a fairly complex process which is partly synthetic ; it is suggested that in addition to the direct oxidation to *apo*caffeine, some dimethylalloxan and methyl-carbamide are produced, the latter substances then condensing to *iso*apocaffeine and *apo*caffeine. In support of this view it is mentioned that only when the oxidation is so moderated as to proceed slowly is any *iso*apocaffeine formed.

When an aqueous solution of *iso*apocaffeine is evaporated to a syrup, isocaffuric acid, $\begin{smallmatrix} NMe\cdot CO \\ CO-NH \end{smallmatrix} >C(OH)\cdot CO\cdot NHMe$, is obtained, which gradually crystallises in prisms, m. p. 191° (decomp.).

When heated on a water-bath with hydriodic acid (D 1·96), *iso*apo-caffeine undergoes reduction to 3-*methylhydantoin-5-carboxymethyl-amide*, $\begin{smallmatrix} NMe\cdot CO \\ CO-NH \end{smallmatrix} >CH\cdot CO\cdot NHMe$, prisms, m. p. 240°. This substance is hydrolysed by barium hydroxide solution with formation of methyl-amine and 3-*methylhydantoin-5-carboxylic acid*, $\begin{smallmatrix} NMe\cdot CO \\ CO-NH \end{smallmatrix} >CH\cdot CO_2H$, tablets, m. p. 130° (decomp.); the latter, on gradually heating to 190°, eliminates carbon dioxide with production of 3-methylhydantoin, $\begin{smallmatrix} NMe\cdot CO \\ CO \end{smallmatrix} >CH_2$.

*iso*apoCaffeine consequently has the structure $\begin{smallmatrix} NMe\cdot CO \\ CO-NH \end{smallmatrix} >C< \begin{smallmatrix} O-CO \\ CO\cdot NMe \end{smallmatrix}$.
    D. F. T.

Some New Salts of Quinine, Euquinine, Aristoquinine, Saloquinine, and Quinaphenine. DECIO ANGELONI (*Boll. chim. farm.*, 1913, **52**, 675—685).—A basic *salicylate* of *quinaphenine*, $C_{20}H_{23}O_2N_2\cdot CO\cdot NH\cdot C_6H_4\cdot OEt,OH\cdot C_6H_4\cdot CO_2H$, has m. p. 125—126°, and is obtained by adding an ethereal solution of the acid to an ethereal solution of an equimolecular quantity of the base. When 2 mols. of acid are taken and the base is poured into the acid, a *salt*, m. p. 112°, is obtained, which is, however, a mixture of the normal and basic salts.

When an ethereal solution of euquinine (1 mol.) is added to an ethereal solution of novaspirin ($\frac{1}{2}$ mol.), the normal *salt*, m. p. 95°, is obtained. By working in alcoholic solution, the basic *salt* may be prepared; it has m. p. 178°.

· Novaspirin and aristoquinine yield the normal *salt*, m. p. 89—90°, in which the aristoquinine behaves as a tetracidic base. Novaspirin and saloquinine in ethereal solution yield the normal *salt*, m. p. 116°. Novaspirin and quinaphenine also yield the normal *salt*, m. p. 118—120°.

Diaspirin and quinine in ethereal solution yield the basic *salt*, which crystallises in needles, m. p. 125°. By taking an excess of acid, the normal *salt* may also be prepared. Diaspirin and quinaphenine in ethereal solution yield the normal *salt*, m. p. 116°.

Diplosal and quinine in ethereal solution yield the basic *salt*, m. p. 105°, which crystallises in needles. Diplosal and quinaphenine in ethereal solution also form the basic *salt*, m. p. 86°.

The compositions of the salts obtained were established by nitrogen estimations. Information is also given as to the solubilities of the bases and acids employed in ether. R. V. S.

The Apparent Colloidal Character and the Molecular Weight of Colchicine. SIMON ZEISEL and K. VON STOCKERT (*Monatsh.*, 1913, 34, 1327—1338).—In aqueous solution, colchicine has many of the physical and physiological properties of a colloid. Diffusion experiments with a 20% solution show, however, that it is a crystalloid. The amyloid of the diffusion thimble has a great adsorptive power for the alkaloid, and until this is satisfied, the diffusion does not reach a normal value. Cryoscopic and ebullioscopic determinations of the molecular weight of colchicine, colchiceine, and trimethylcolchicinic acid in various solvents have also been made. In acetic acid or boiling ethylene dibromide, the results for colchicine agreed with the formula $C_{22}H_{25}O_6N$. In cold ethylene dibromide and especially in water, which is most unusual, bi- or even ter-molecular values were obtained. Colchiceine gave high values in freezing ethylene dibromide, and trimethylcolchicinic acid in boiling acetic acid.

J. C. W.

Bromine Derivatives of Colchicine. SIMON ZEISEL and K. VON STOCKERT (*Monatsh.*, 1913, 34, 1339—1347).—When an excess of hydrobromic acid is added to a dilute solution of colchicine, sulphur-yellow *dibromocolchicine*, $C_{22}H_{23}O_6NBr_2$, is precipitated, m. p. 146—150° (open tube), 125° (sealed capillary). One molecular proportion of the acid precipitates the *monobromide*, which crystallises in various forms from methyl alcohol, but with constant properties,

$$C_{22}H_{24}O_6NBr,MeOH,$$
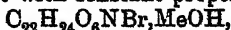
m. p. 151·5° (corr., open tube), 133—135° (sealed tube). It is somewhat soluble in water, and the addition of excess of hydrobromic acid to the aqueous mother liquors causes the precipitation of the above dibromide. In methyl alcohol solution, colchicine gives with excess of bromine in the cold, a *tribromide*, $C_{18}H_{10}(OMe)_4O_2NBr_3$, m. p. 131° (open), 118—122° (sealed). The behaviour of these derivatives

towards alkali hydroxides, in open vessels or in sealed tubes, shows that two bromine atoms are firmly combined, whilst the third is fairly labile. *Tribromocolchiceine*, $C_{21}H_{20}O_6NBr_3,H_2O$, and *tribromotrimethyl-colchicinic acid*, $C_{19}H_{18}O_5NBr_3$, were also prepared.   J. C. W.

Synthesis of Hygrine. I. KURT HESS (*Ber.*, 1913, 46, 3113—3125).—Hygrine should have either the constitution I or II.

(I) $CH_2 <^{CH_2 \cdot NMe \cdot}_{CH_2 \cdot CH \cdot COEt}$ (II) $CH_2 <^{CH_2 \cdot NMe}_{CH_2 \cdot CH \cdot CH_2 \cdot COMe}$
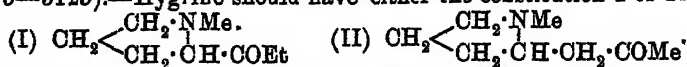
Willstätter (A., 1900, i, 405) suggested that the second formula was probable, assuming, therefore, that hygrine and tropinone are somewhat similarly constituted, but the fact that the oxidation product, hygric acid (Liebermann and Cybulski, A., 1895, i, 310 ; Willstätter, *loc. cit.*, and A., 1903, i, 362), is not an acetic acid derivative akin to tropic acid supports formula I. The author has attempted to synthesise the above isomerides, and has so far succeeded in preparing the corresponding hydroxy-compounds :

(III) $CH_2 <^{CH_2 \cdot NMe}_{CH_2 \cdot CH \cdot CHEt \cdot OH}$ (IV) $CH_2 <^{CH_2 \cdot NMe}_{CH_2 \cdot CH \cdot CH_2 \cdot CHMe \cdot OH}$
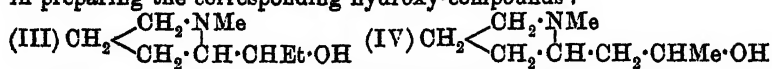
The former compound was obtained by treating magnesium pyrryl bromide with propionyl chloride, reducing the 2-propionylpyrrole so obtained by sodium and alcohol, and methylating the product. The other compound was prepared by the addition of propylene oxide to magnesium pyrryl bromide, reduction of the *iso*propyl alcohol derivative by means of hydrogen in presence of spongy platinum, and methylation of the pyrrolidyl-2-*iso*propyl alcohol.

α-2-Pyrrylpropan-β-ol, $C_4H_4N \cdot CH_2 \cdot CHMe \cdot OH$, is a colourless, odourless, viscous oil, b. p. 94—96°/0·25 mm., which changes into a thick, red syrup in the air, and is soluble in water. No picrate nor oxidation product could be isolated, but it yielded 2-propylpyrrole (Dennstedt and Zimmermann, A., 1893, i, 226) on reduction with red phosphorus and hydriodic acid. It was accompanied by an isomeride, probably, $CH <^{CH \cdot NH}_{CH:C \cdot CHMe \cdot CH_2 \cdot OH}$, which had b. p. 99—107°/ 0·25 mm.

For the methylation, it was found necessary to prepare the potassium compound and then to add methyl iodide. *α-1-Methyl-pyrrylpropan-β-ol*, $C_8H_{13}ON$, is a pleasant smelling oil, b. p. 116—117°/18 mm. The reduction of pyrrylpropan-β-ol with hydrogen in presence of platinum was successful when the necessity of excluding all traces of oxygen was realised. For this purpose an apparatus is described which consists essentially of a cylinder and bulb connected by a tap, the cylinder being also fitted with an inlet tube and a ground-on cap. The suspension of platinum in glacial acetic acid was saturated with hydrogen in the bulb, the solution of the alcohol was then washed with hydrogen in the cylinder, and finally the two liquids were shaken together under a slightly increased pressure. The platinum was not added all at once, but fresh portions were occasionally saturated with hydrogen in the cylinder and then allowed to flow into the bulb. The process required a few days. In

this way the formation of pyrrole dyes by catalytic oxidation was entirely prevented, and only a small quantity of platinum was required. A quantitative reduction of pyrrole itself, without the occurrence of a coloured solution, was also effected (compare Willstätter and Hatt, A., 1912, i, 545). *α-2-Pyrrolidylpropan-β-ol*, $C_4H_8N \cdot CH_2 \cdot CHMe \cdot OH$, is a viscous oil, b. p.115—120°/15 mm.,with the usual properties of a base and an unsaturated compound. On methylation with methyl iodide and potassium hydroxide, a moderate yield of *α-1-methylpyrrolidylpropan-β-ol* (IV) was obtained as an oil, b. p. 98—103°/16 mm.

2-Pyrrylpropane-βγ-diol (future communication) was also reduced as above, yielding *α-2-pyrrolidylpropane-βγ-diol*

$$C_4H_8N \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH,$$
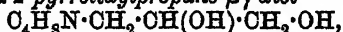
b. p. 145—150°/18 mm., which formed a very hygroscopic potassium salt.

The reduction of the isomeric alcohols was first studied in the case of 2-acetylpyrrole. Sodium was added to the boiling alcoholic solution of the substance and *α-2-pyrrolidylethan-α-ol (pyrrolidyl-2-methylcarbinol)*, $C_4H_8N \cdot CHMe \cdot OH$, was extracted from the product as a colourless oil, b. p. 187—192°/759 mm. It smells like acetamide and absorbs moisture and carbon dioxide with avidity. *α-2-Pyrrolidylpropan-α-ol (pyrrolidyl-2-ethylcarbinol)*, $C_4H_8N \cdot CHEt \cdot OH$, was prepared in this way from 2-propionylpyrrole. It is a well-defined, crystalline base, m. p. 50°, b. p. 95—98°/17 mm., 195—200°/756 mm., with a narcotic odour, is hygroscopic, and gives the Liebermann reaction. *α-1-Methylpyrrolidylpropan-α-ol (1-methylpyrrolidyl-2-ethylcarbinol)* (III.) is also a very hygroscopic base, m. p. 45°, b. p. 92—95°/17 mm., 190—195°/757 mm. J. C. W.

Origin of the Cyclic Bases of Coal-tar. LOUIS C. MAILLARD (*Compt. rend.*, 1913, **157**, 850—852).—The humic substances obtained by the condensation of sugars with different amino-acids (compare A., 1912, i, 169) readily yield cyclic bases when heated. The author applies this to the formation of coal from the constituents of cellulose and proteins and to its distillation, yielding coal-tar containing pyridine and other cyclic bases. W. G.

Allylpyrroles. KURT HESS (*Ber.*, 1913, **46**, 3125—3129).—When magnesium pyrryl bromide is treated with allyl bromide, a mixture of approximately equal quantities of 2-allyl- and 2 : 5-diallyl-pyrroles is obtained. The formation of the latter compound is explained by assuming that some magnesium pyrryl bromide reacts with 2-allyl-pyrrole, forming pyrrole and 5-magnesium-2-allylpyrryl bromide, which then unites with more allyl bromide. This view is supported by the fact that carbon dioxide converts the reaction product of 2-allylpyrrole and magnesium pyrryl bromide into 2-allylpyrryl-5-carboxylic acid, acid, from which it follows that allylpyrrole is more acidic than pyrrole.

The reaction between allyl bromide and magnesium pyrryl bromide

was vigorous but was not moderated by cooling. After steam distillation and extraction with ether, 2-*allylpyrrole*,

$$CH<_{CH:C\cdot CH_2\cdot CH:CH_2}^{CH\cdot NH},$$
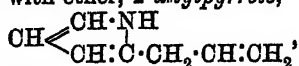
was obtained as a colourless, mobile liquid, b. p. 82—83°/24 mm., D_4^{24} 0·9376. It has an unpleasant odour, rapidly becomes yellow in the air, finally forming a red, amorphous mass, and is extremely sensitive towards reagents. 2 : 5-Diallylpyrrole, $C_4H_8N(CH_2\cdot CH:CH_2)_2$, is a similar liquid, b. p. 110—115°/17 mm., D_4^{24} 0·9321. The addition of allylpyrrole to magnesium pyrryl bromide caused a change in colour from grey to dark green. After treatment with dry carbon dioxide,

2-*allylpyrrylcarboxylic acid*, $CH<_{CH==C\cdot CH_2\cdot CH:CH_2}^{C(CO_2H)\cdot NH}$, was obtained in indefinite crystals, m. p. 117—118°. It is unstable, and partly decomposes into violet-pink dyes even when boiled with light petroleum.   J. C. W.

Equilibrium in the System Cobalt Chloride and Pyridine. J. NEWTON PEARCE and T. E. MOORE (*Amer. Chem. J.*, 1913, **50**, 218—231).—In order to investigate the formation of compounds of cobalt chloride with pyridine of crystallisation, a study has been made of this system by the solubility method at temperatures between −50·3° and 100°. The results show the existence of three distinct crystalline compounds, $CoCl_2,2C_5H_5N$; $CoCl_2,4C_5H_5N$, and $CoCl_2,6C_5H_5N$. The first two of these have been isolated previously by Reitzenstein (A., 1895, i, 121). The compound $CoCl_2,2C_5H_5N$ has m. p. 195—200°, but the m. p.'s of the other two compounds cannot be ascertained, as they rapidly lose pyridine when heated under the ordinary pressure.

The compound $CoCl_2,6C_5H_5N$ exists as the solid phase between −50·3° and 15°, $CoCl_2,4C_5H_5N$ between 15° and 70°, $CoCl_2,2C_5H_5N$ between 70° and 90°, whilst between 90° and the b. p. of the saturated solution $CoCl_2$ is the stable, solid phase.

The usual methods of estimating cobalt are not satisfactory in presence of pyridine, and the following method was therefore devised. The weighed sample of solution was heated at 120° until all the pyridine had been removed. It was then dissolved in 50% alcohol, and an excess of oxalic acid was added to the solution. The precipitated cobalt oxalate was washed with 50% alcohol, dried at 100°, and dissolved in sulphuric acid (1 : 3). The solution was diluted to 300 c.c., heated nearly to boiling, and titrated with potassium permanganate. This method was found to be very accurate.   E. G.

Cyclic Imines. VIII. Ring Opening in Substituted Indoles and Quinolines. JULIUS VON BRAUN, ALFRED GRABOWSKI, and MARGARETE RAWICZ (*Ber.*, 1913, **46**, 3169—3182).—A number of cyclic imines (substituted quinoline and indole derivatives) have been converted into compounds of the phenylpropane series primarily to determine with what yield the chlorinated amides could be obtained on treating the *N*-benzoyl compounds of the imines with phosphorus pentachloride, and to study the hydrolysis of these amides to the

chlorinated bases. It appears that the substituted anilides are formed even more readily than the unsubstituted compounds previously described, and they are readily purified from unchanged imine. They are hydrolysed with difficulty as the temperatures necessary to ensure hydrolysis and at which decomposition begins lie very near together.

6-*Chlorotetrahydroquinoline*, $C_6H_8Cl\begin{smallmatrix}CH_2 \cdot CH_2\\NH-CH_2\end{smallmatrix}$, obtained by reduction of 6-chloroquinoline and isolated by means of the benzoyl compound, has b. p. 160°/11 mm., m. p. 43°. The *hydrochloride* crystallises in lustrous needles, m. p. 190°; the *platinichloride* is yellow, m. p. 185°. The *benzoyl* derivative has m. p. 84°. The *picrate*, m. p. 151°, and the *nitroso*-compound, m. p. 65°, are also described.

On heating the benzoyl derivative with phosphorus pentachloride at 140°, *benzo*-p-γ-*dichloro*-o-*propylanilide*,

$$CH_2Cl \cdot CH_2 \cdot CH_2 \cdot C_6H_3Cl \cdot NH \cdot COPh,$$
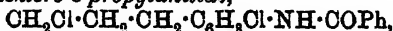
is obtained in a mass of snow-white crystals, m. p. 108°. On prolonged heating with concentrated hydrochloric acid at 125°, p-γ-*dichloro*-o-*propylaniline hydrochloride* is obtained, m. p. 170°. The free base, $C_3H_6Cl \cdot C_6H_3Cl \cdot NH_2$, is a slightly coloured, almost odourless oil. The yellow *platinichloride*, has m. p. 181—182°, and the *picrate* has m. p. 143°.

On diazotisation and treatment with cuprous chloride, 2 : 5-γ-*trichloropropylbenzene*, $C_6H_3Cl_2 \cdot C_3H_6Cl$, is obtained as a colourless oil of agreeable odour, b. p. 152°/16 mm.

7-*Nitrotetrahydroquinoline*, $NO_2 \cdot C_6H_3\begin{smallmatrix}CH_2 \cdot CH\\NH \cdot CH_2\end{smallmatrix}$, prepared by nitrating tetrahydroquinoline in concentrated sulphuric acid, forms a yellowish-red, crystalline mass, m. p. 90°. The *hydrochloride* separates in colourless needles, m. p. 203°; the colourless *benzoyl* derivative has m. p. 141°, whereas the *nitroso*-compound has m. p. 118—120°.

On opening the ring with phosphorus pentachloride, *benzo*-γ-*chloro*-5-*nitro*-2-*propylanilide*, $C_3H_6Cl \cdot C_6H_3(NO_2) \cdot NHBz$, is obtained in well formed, colourless needles, which are converted on hydrolysis at 120° into γ-*chloro*-5-*nitro*-2-*propylaniline*, a red compound, m. p. 76°. The *hydrochloride* has m. p. 217°, the *platinichloride* forming a yellow, crystalline precipitate.

Heating with dimethylamine converts the benzonitroanilide into *benzo*-γ-*dimethylamino*-5-*nitro*-2-*propylanilide*,

$$NMe_2 \cdot C_3H_6 \cdot C_6H_3(NO_2) \cdot NHBz,$$
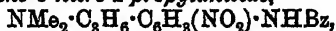
crystallising in well formed, colourless needles, m. p. 157°. The *hydrochloride* and *picrate* are oily.

γ-*Dimethylamino*-5-*nitro*-2-*propylaniline*, obtained on hydrolysis, separates in yellow crystals, m. p. 65—66°. The *dihydrochloride* has m. p. 191°, and the *dipicrate*, m. p. 146°.

6-*Chloro*-7-*nitrotetrahydroquinoline* forms red crystals, m. p. 84°. The *hydrochloride*, m. p. 184°, becomes red in presence of moisture. The yellow *nitroso*-derivative has m. p. 124°, and the *benzoyl* derivative has m. p. 126°.

Dichlorobenzo-4-γ-*dichloro*-5-*nitro*-2-*propylanilide* is colourless, m. p. 173—174°. Hydrolysed at 120—125° it forms 4-γ-*dichloro*-5-*nitro*-2-

propylaniline : this is yellow, m. p. 90°, and forms a colourless *hydrochloride*, m. p. 150—151°, which becomes bright yellow when wet.

7-*Benzoylaminotetrahydroquinoline*, m. p. 189°, forms a *platinichloride*, m. p. 280—282°.

7-*Aminotetrahydroquinoline*, obtained either on hydrolysis of the above or by reducing the corresponding nitro-compound, forms a colourless oil, b. p. 195°/15 mm., m. p. 60°. The *hydrochloride*, m. p. 240°, and the *dibenzoyl* derivative, m. p. 233°, are described. The 2 : 3-*dibenzoylamino-γ-chloropropylbenzene*,

$$C_3H_6Cl \cdot C_6H_3(NHBz)_2,$$
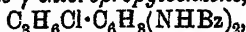
obtained from this has m. p. 198—200°, forming a colourless powder.

The *acetyl* derivative, $NHAc \cdot C_6H_3 \diagup \substack{CH_2-CH_2 \\ NMe \cdot CH_2}$, of 7-aminokairoline, m. p. 114°, when treated with cyanogen bromide forms 1-*cyano-7-acetylaminotetrahydroquinoline*, m. p. 152°, which is hydrolysed to 7-*aminotetrahydroquinoline*, m. p. 60°.

6-*Nitrodihydroscatole*, $NO_2 \cdot C_6H_3 \diagup \substack{CHMe \\ NH} \diagdown CH_2$, from dihydroscatole, has m. p. 75°; the *hydrochloride* has m. p. 192°, the yellow *nitroso*-compound has m. p. 100°, and the *benzoyl* derivative, which crystallises in lustrous platelets, has m. p. 148°. *Benzo-5-nitro-2-β-chloro*isopropylanilide, $NHBz \cdot C_6H_3(NO_2) \cdot CHMe \cdot CH_2Cl$, crystallises in colourless, matted needles, m. p. 110°. Hydrolysis at 125° converts it into *nitrodihydroscatole hydrochloride*, m. p. 192°.

6-*Nitrodihydromethylindole*, $NO_2 \cdot C_6H_3 \diagup \substack{CH_2 \\ NH} \diagdown CHMe$, has m. p. 50°, and forms a *benzoyl* compound, m. p. 137°, a *hydrochloride*, m. p. 200° after sintering previously, and a nitroso-compound, m. p. 103—104°. *Benzo-5-nitro-2-β-chloropropylanilide*,

$$PhCO \cdot NH \cdot C_6H_3(NO_2) \cdot CH_2 \cdot CHMeCl,$$
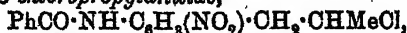
is colourless, m. p. 150°, and is converted on hydrolysis into 5-*nitro-2-β-chloropropylaniline*, a yellowish-red, crystalline mass, m. p. 84°. Treatment with dimethylamine converts it into 2-β-*benzo-5-nitro-2-dimethylaminopropylanilide*, $NO_2 \cdot C_6H_3(NHBz) \cdot CH_2 \cdot CHMe \cdot NMe_2$, crystallising in colourless needles, m. p. 122°. The analogous *piperidino*-compound, $NO_2 \cdot C_6H_3(NHBz) \cdot CH_2 \cdot CHMe \cdot NC_5H_{10}$, has m. p. 117°. E. F, A.

Action of Phosphoric Oxide on Benzylideneacetoneoxime. H. BURSTIN (*Monatsh.*, 1913, **34**, 1443—1448).—Goldschmidt (A., 1895, i, 392) by warming benzylideneacetoneoxime with phosphoric oxide could only isolate *iso*quinoline, whereas 2-methylquinoline or 1-methyl*iso*quinoline would represent a normal course for the condensation. The author has obtained a similar product, b. p. 240—250°, which gave a platinichloride, and corresponded with a mixture of the homologous quinolines. By the formation of quinophthalone (Jacobsen and Reimer, A., 1883, i, 812) and quinoline-2-carboxylic acid (Koenigs, A., 1899, i, 390), the presence of 2-methylquinoline was proved, whilst the formation of *iso*quinoline-red (Vongerichten and Homann, this vol., i, 99) indicated the presence of a mixture of 2-methylquinone and *iso*quinoline. J. C. W.

Condensation of Phenyl*iso*oxazolone with Ethyl Mesoxalate. ANDRÉ MEYER (*Bull. Soc. chim.*, 1913, [iv], **13**, 903—909).—By the condensation of these two products it was expected that coloured substances of the general formula $\begin{matrix} \text{N:CPh} \\ | \quad \quad \\ \text{O—CO} \end{matrix}\!\!>\!\!\text{O:C(CO·R)·CO}_2\text{R}'$ would be produced, but instead it was found that two molecules of phenyl-*iso*oxazolone took part in the reaction with the formation of compounds of the type $\begin{matrix} \text{N:CPh} \\ | \quad \quad \\ \text{O—CO} \end{matrix}\!\!>\!\!\text{CH·C(CO}_2\text{R)}_2\text{·CH}\!\!<\!\!\begin{matrix} \text{CPh:N} \\ \quad \quad | \\ \text{CO—O} \end{matrix}$, or their enolic forms.

*Ethyl mesoxalate bisphenyl*isooxazolone [*Bis-3-phenyl*isooxazolone-4-malonate], m. p. 187° (decomp.), forms large octahedra by slow evaporation of its solutions or small, prismatic crystals from acetic acid or boiling alcohol; it is soluble in alkalis and can be titrated, 1 mol. requiring 2 mols. of alkali to produce neutrality in presence of phenolphthalein. The sodium *salt* is crystalline and hygroscopic; those of the heavy metals are colourless and amorphous; ferric chloride gives a violet precipitate.

The sodium salt with ethyl iodide furnishes the *diethyl ether*, m. p. 200—201°, crystallising in silky, slender needles. The *diacetyl* derivative, m. p. 165—166°, forms small, prismatic crystals, and the *dibenzoyl* derivative, m. p. 194°, colourless leaflets or stellate groups of prismatic needles. Cryoscopic determinations of the molecular weight of the latter gave abnormal results. With benzenediazonium chloride, ethyl bis-3-phenyl*iso*oxazolone-4-malonate gave benzeneazo-phenyl*iso*oxazolone.   T. A. H.

The Constitution of Dinitrothiodiphenylamine [Dinitrophenthiazine]. FRIEDRICH KEHRMANN and FERD. RINGER (*Ber.*, 1913, **46**, 3014—3020. Compare Möhlau, Beyschlag, and Köhres, A., 1912, i, 212).—The authors believe that the dinitrophenthiazine obtained by Möhlau and his collaborators (*loc. cit.*) by the condensation of picryl chloride with *o*-benzoylaminophenyl mercaptan and subsequent treatment with sodium hydroxide solution is actually identical with and not an isomeride of the 3 : 5-dinitrophenthiazine described by Kehrmann and Schild (A., 1900, i, 61). In spite of the presence of the benzoyl radicle, the picryl chloride must therefore have made the amino-group and not the mercaptan group its main point of attack. In the action of picryl chloride on free aminophenyl mercaptan as well as on its benzoyl derivative, however, by-products are obtained which probably represent the isomerides of the main products and have the picryl radicle attached at the sulphur atom.

The compound, golden-yellow prisms, m. p. 169°, which is the main product of the interaction of picryl chloride and *o*-benzoylaminophenyl mercaptan, is therefore considered to have the structure

$$\text{SH·C}_6\text{H}_4\text{·NBz·C}_6\text{H}_2(\text{NO}_2)_3,$$
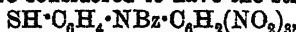
that is, *benzo*-2 : 4 : 6-*trinitro*-2'-*thioldiphenylamide*, whilst the substance, orange-yellow, leafy crystals, m. p. 142°, which results in smaller quantity, is probably the true trinitrophenyl *o*-benzoylaminophenyl sulphide. If the former substance, m. p. 169°, dissolved in alcohol is

treated with dilute sodium hydroxide solution and left at the ordinary temperature, there slowly separates 3 : 5-*dinitro*-6-*benzoylphenthiazine*, $C_6H_4{<}^{NBz}_{S}{>}C_6H_2(NO_2)_2$, straw-yellow leaflets, m. p. 209°, which on hydrolysis by alcoholic sodium hydroxide undergoes conversion into 3 : 5-dinitrophenthiazine, m. p. 188—190°, identical with the product of Kehrmann and Steinberg (A., 1911, i, 1034) ; the m. p. 218°, observed by Möhlau and his collaborators, must be due either to the occurrence of dimorphism or to the presence of impurities.

The substance described by Möhlau as 2 : 4-diaminophenazthionium ferrichloride (*loc. cit.*) is in reality the ferrichloride of 3 : 5-diaminophenazthionium, the experimental conditions deciding whether the ferrichloride or merely the chloride (Kehrmann and Schild, *loc. cit.*) shall separate.

When a suspension of 3 : 5-dinitrophenthiazine in cold acetic acid is gradually treated with powdered sodium nitrite (compare this vol., i, 1231), the substance passes into solution and there separates 3 : 5 : 9-*trinitrophenthiazine* (annexed formula), brownish-red, lustrous prisms, m. p. 214°. This substance by reduction in alcoholic solution by stannous chloride and hydrochloric acid, followed by oxidation of the separated, colourless *zincochloride* with ferric chloride, passes into 3 : 5 : 9-*trinitrophenazthionium chloride*, long needles with a metallic green lustre ; *nitrate*, sparingly soluble ; *platinichloride*, violet-black, crystalline powder.

The identity of the dinitrophenthiazine resulting from the methods of the two above-mentioned groups of investigators was further confirmed by energetic nitration, when 3 : 5 : 7 : 9-tetranitrodiphenylaminesulphoxide (annexed formula) was obtained in each case as well as in the nitration of 3 : 9-dinitro- and of 3 : 5 : 9-trinitro-phenthiazine.

A closer examination of the reaction product from *o*-aminophenyl mercaptan and picryl chloride reveals the presence of a small quantity of a *substance*, straw-yellow tablets, in addition to the 2 : 4 : 6-trinitro-2'-thioldiphenylamine which was described earlier. It is believed that the former is possibly trinitrophenyl aminophenyl sulphide.   D. F. T.

Preparation of *N*-Alkyl-*p*-phenylenediaminesulphonic Acids CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (D.R.-P. 264927).— *N*-Alkyl-*p*-phenylenediaminesulphonic acids are obtained by the action of neutral alkali sulphites on *p*-nitroso-compounds of secondary or tertiary amines of general formula $NO\cdot R\cdot NR_1R_2$, where R is phenyl or a homologue of the same, R_1 hydrogen, alkyl or alkylaryl, and R_2 alkyl or alkylaryl.

p-*Phenylene*-as-*dimethyldiaminesulphonic acid*, $C_8H_{12}O_3N_2S$ (in which the sulphonic group is probably ortho- to the primary amino-group), is obtained when an aqueous solution of *p*-nitrosodimethylaniline (10 parts) is slowly treated at the ordinary temperature with a solution

of sodium sulphite (30 parts), and when the nitroso-compound has completely dissolved the mixture boiled with concentrated hydrochloric acid (90 parts); the acid is extremely soluble in water, but can be purified and finally isolated by means of its crystalline *benzylidene* derivative.

p-*Phenylene-as-diethyldiaminesulphonic acid* (prepared from nitrosodiethylaniline) is more readily isolated in crystalline form, whilst p-*phenylene-as-benzylethyldiaminesulphonic acid* furnishes a sparingly soluble *sodium* salt.

o-*Tolylene-2-ethyldiaminesulphonic acid* is obtained in a similar manner from *p*-nitrosoethyl-*o*-toluidine, and is isolated through its *benzylidene* derivative.   F. M. G. M.

Leuco-bases and Colouring Matters Derived from Diphenylethylene. VI. The First Stage in the Oxidation of the *cyclo*Hexylidene **Leuco-base,** $C_6H_{10}:C[C_6H_4\cdot NMe_2]_2$. **Tetrahydromalachite-green.** PAUL LEMOULT (*Compt. rend.*, 1913, **157,** 597—599. Compare A., 1912, i, 791).—Tetramethyldiaminodiphenyl-*cyclo*hexylidenemethane (formula I), when acted on by lead peroxide, gives a bluish-coloured substance, which spontaneously decomposes in aqueous solution, giving the compound (formula III) having two atoms of hydrogen less than the initial leuco-base (compare *loc. cit.*):

$$\text{(I.) } CH_2 {\textstyle \begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}} C:C(C_6H_4\cdot NMe_2)_2$$

(II.) $C_6H_9\cdot C(OH)(C_6H_4\cdot NMe_2)_2$ (III.) $C_6H_8:C(C_6H_4\cdot NMe_2)_2$.
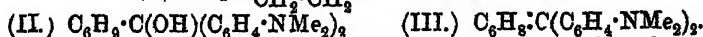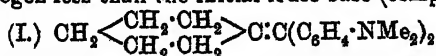
The author has now succeeded in isolating the unstable substance (formula II) by precipitating it from acid solution with ammonia, drying it in a vacuum over sulphuric acid, followed by crystallisation from benzene. Heated slowly, it has m. p. 130—135°, heated rapidly, m. p. 160°, whilst the instantaneous m. p. is 145°. If the liquid is allowed to cool and re-melted it has m. p. 165°, which is in accord with elimination of water, giving substance III, m. p. 169° (*loc. cit.*). This transformation is also brought about by simple crystallisation from hot alcohol.

The oxygenated compound on solution in cold alcohol to which one drop of acetic acid has been added, gives a persistent, deep blue solution, thus differing from substances I and II, and in slightly acid solution it dyes cotton, mordanted with tannin, a tint comparable to that given by malachite-green, but appreciably bluer. The absorption spectra of these two compounds, however, show marked differences.
                                                                        W. G.

Leuco-bases and Colouring Matters of Diphenylethylene. VII. Action of Magnesium Methyl and Ethyl Iodides on Michler's Ketone. PAUL LEMOULT (*Compt. rend.*, 1913, **157,** 724—726).—A repetition of Fecht's experiments on the action of magnesium methyl and ethyl iodides on Michler's ketone (compare A., 1907, i, 926). Contrary to Fecht's statements, but in agreement with the results of Freund and Mayer (compare A., 1906, i, 384), the author obtained no carbinols of the type $OH\cdot CMe(C_6H_4\cdot NMe_2)_2$, but a mixture of substances from which he separated unchanged ketone,

an ethylenic derivative of the type $CH_2:C(C_6H_4\cdot NMe_2)_2$, and in the case of magnesium methyl iodide, small quantities of a *substance*, crystallising in yellow needles, m. p. 157—158°, having the composition $C_{18}H_{22}N_2$, but a molecular weight corresponding to twice this, together with two other basic substances, crystallising (*a*) in yellow plates, m. p. 227°, and (*b*) in yellow crystals, m. p. 274°, the constitutions of which have not yet been determined. In the case of magnesium ethyl iodide, no substances corresponding with the last three were found, but a 90% yield of the ethylenic compound, $CHMe:C(C_6H_4\cdot NMe_2)_2$, was obtained.   W. G.

Ditertiary Hydrazines. XVI. Mechanism of the Blue Colour Reaction of Diphenylamine. HEINRICH WIELAND [with CARL MÜLLER] (*Ber.*, 1913, **46**, 3296—3303).—The blue coloration formed in sulphuric acid solutions of diphenylamine by oxidising agents was considered to be an acid sulphate of diphenyl dihydrophenazonium. Kehrmann and Micewicz (A., 1912, i, 1020) have shown that it is more probably a quinonoid derivative of diphenylbenzidine, $PhN:C_6H_4\cdot C_6H_4:NHPh\cdot O\cdot SO_3H$. This explanation is now accepted, although it is not applicable to the colour reactions obtained with diphenylhydrazine, diphenylhydroxylamine, and *p*-dianisylamine.

Diphenylamine in dilute sulphuric acid and acetic acid solution is readily oxidised to the blue dye, which is easily reduced without the formation of by-products to diphenylbenzidine. Tetramethylhydrazine gives only small quantities of diphenylbenzidine as well as amorphous products; its formation cannot, therefore, be regarded as an intermediate stage in the colour reaction.

Triphenylamine shows a similar blue coloration on oxidation, when quinonoid salts of tetraphenylbenzidine are formed. *Tetraphenylbenzidine* crystallises in pale yellow needles, m. p. 226°, to a brownish-yellow liquid.

s-*Diphenyl*-o-*phenylenediamine*, $C_6H_4(NHPh)_2$, obtained by the action of iodobenzene and copper powder on *o*-aminodiphenylamine, crystallises as colourless double pyramids, m. p. 152·5°. On attempting to combine it with *o*-dibromobenzene to diphenyldihydrophenazine, only amorphous products were obtained.   E. F. A.

Ditertiary Hydrazines. XVII. Diphenylhydroxylamine and Some Colour Reactions Related to the Blue Diphenylamine Reaction. HEINRICH WIELAND and CARL MÜLLER (*Ber.*, 1913, **46**, 3304—3314).—Diphenylhydroxylamine reacts with 75% sulphuric acid to form 70% of diphenylbenzidine, together with a little diphenylamine and a green dye of high molecular complexity. The quinonoid-blue salt is formed in this instance by direct elimination of water from diphenylhydroxylamine. When the sulphuric acid is diluted with acetic acid instead of water, the anhydro-product obtained is carbazole together with considerable quantities of *p*-hydroxydiphenylamine.

Even ice-cold sulphuric acid converts diphenylhydrazine into diphenylhydroxylamine, which is converted into diphenylbenzidine

as described. Much ammonia is also formed, also traces of *o*-amino-diphenylamine and some *p*-hydroxydiphenylamine.

p-Tolylhydrazine and concentrated sulphuric acid give at first a bluish-green and green coloration due to hydroxylamine, and ammonia is also formed. Further decomposition yields a yellowish-brown, amorphous substance and much ditolylamine.

Tetraphenyl- and *p*-tetratolyl-hydrazine dissolve in sulphuric acid with a reddish-violet coloration which changes to blue. Diphenylamine and ditolylamine are also formed respectively.

On oxidation of *p*-dianisylamine with persulphate and sulphuric acid, the salt, $OMe \cdot C_6H_4 \cdot N \vdots C_6H_4 \vdots OMe \cdot O \cdot SO_3H$, is first formed, but could not be isolated. A blue sulphate of the character of an indophenol which is red in solution was obtained; it very readily yields *p*-benzoquinone on treatment with dilute acids, and is considered to be the acid sulphate of a polymerised bimolecular *anisylquinone monoimine*,

$$HO \cdot C_6H_4 \cdot N(C_6H_4 \cdot OMe) \cdot C_6H_3(OMe) \cdot N \vdots C_6H_4O.$$
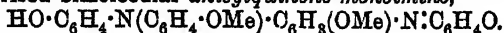
E. F. A.

The Action of Organomagnesium Compounds on Diazomethane and Ethyl Diazoacetate. II. ERNST ZERNER (*Monatsh.*, 1913, **34**, 1631—1638. Compare this vol., i, 1312).—The author makes some observations on the paper by Forster and Cardwell (T., 1913, **103**, 86) on the constitution of aliphatic diazo-compounds, and describes the preparation of benzaldehydephenylhydrazone by the action of diazomethane on magnesium phenyl bromide. The formation of this compound is assumed to follow the course:

$$CH_2 \vdots N \cdot N + PhMgBr \longrightarrow CH_2 \vdots N \cdot NPh \cdot MgBr + PhMgBr \longrightarrow$$
$$CH_2Ph \cdot NMgBr \cdot NPh \cdot MgBr \longrightarrow CH_2Ph \cdot NH \cdot NH \cdot CH_2Ph \longrightarrow$$
$$CHPh \vdots N \cdot NHPh.$$
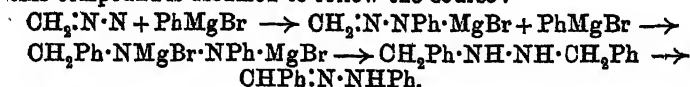
The ring formula for the fatty diazo-compound would require that at least one nitrogen atom would be involved in the addition of two molecules of the magnesium compound, which is contrary to experience.

J. C. W.

The Condensation of Ethyl Oxalate with Pyrazolones. WILHELM WISLICENUS, HEINRICH ELVERT, and PAUL KURTZ (*Ber.*, 1913, **46**, 3395—3407).—On the addition of a benzene solution of phenylmethylpyrazolone (prepared from ethyl acetoacetate) to a mixture of ethyl oxalate and potassium ethoxide dissolved in ether, there separates slowly the *potassium* derivative, yellowish-white crystals, decomp. between 138° and 145°, of *ethyl 1-phenyl-3-methyl-5-pyrazolone-4-glyoxylate*, $CO_2Et \cdot CO \cdot CH \begin{smallmatrix} CO-NPh \\ OMe \cdot N \end{smallmatrix}$, yellowish-white needles, m. p. 81—82°, which can be liberated by addition to cold dilute hydrochloric acid; the ester gives a deep red coloration with ferric chloride and also with common benzene and sulphuric acid; its tendency to enolisation is further evidenced by the formation of a green *copper* derivative, m. p. 220—223°, and of an *ammonium* derivative, m. p. 120—123° (decomp.). Treatment of the ester with phenylcarbimide caused the formation of the *carbanilate* of *ethyl 1-phenyl-3-methyl-5-pyrazolol-4-gly-*

oxylate, $N{<}^{NPh-C\cdot O\cdot CO\cdot NHPh}_{\ CMe-C\cdot CO\cdot CO_2Et}$, colourless needles, m. p. 97°, which
like the corresponding additive compound from phenylcarbimide and
phenylmethylpyrazolone, namely, 1-*phenyl-3-methyl-5-pyrazolyl carb-
anilate*, colourless needles, m. p. 92—93°, is unstable, and when
heated gives an odour of phenylcarbimide.

Ethyl phenylmethylpyrazoloneglyoxylate gives a *phenylhydrazone*,
almost colourless needles, m. p. 182—183°, in the formation of which a
difficultly isolable *isomeride*, yellow leaflets, is also produced ; p-*bromo-
phenylhydrazone*, yellowish-white needles, m. p. 213—214°.

1-*Phenyl-3-methyl-5-pyrazolone-4-glyoxylic acid*, yellowish-white
needles, m. p. 236—238°, is obtainable by hydrolysis of the ester.
With sulphuric acid it gives on warming a green coloration changing
successively to red and brown, and at 200° it is converted with loss of
carbon dioxide into the already known phenylmethylpyrazolone-
sulphonic acid (Möllenhoff, A., 1892, 1245). Heated with aniline
at 150°, the acid gives rise to the *anil* of 1-*phenyl-3-methyl-5-pyrazolone-
4-aldehyde*, greenish-yellow needles, m. p. 151—152°. The acid reacts
slowly with phenylhydrazine in alcoholic solution at the ordinary tem-
perature, giving rise to a *phenylhydrazone*, almost colourless needles,
m. p. 205—206°, which can be esterified by alcohol and hydrogen
chloride to the previously mentioned phenylhydrazone of the ester. If
phenylmethylpyrazoloneglyoxylic acid is heated with methyl or ethyl
alcohol for an hour in a sealed tube at 160—180°, orange-yellow
needles of 1-phenyl-3-methyl-4-methylene-5-pyrazolone,

$$\begin{matrix} NPh-CO \\ N=CMe \end{matrix}{>}C{:}CH_2,$$
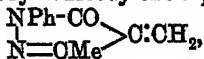
separate (compare Pellizzari, A., 1889, 517), a small amount of a
colourless *substance*, m. p. above 280°, which in alcoholic solution gives
a violet precipitate with ferric chloride being present in the mother
liquor.

1 : 3-Diphenyl-5-pyrazolone condenses with ethyl oxalate under the
same conditions as the above methylpyrazolone, giving the *sodium* or
potassium derivatives of *ethyl 1 : 3-diphenyl-5-pyrazolone-4-glyoxylate*,
which after acidifying is obtainable in yellowish-white, prismatic needles,
m. p. 108—109°. The ester, which gives similar colour reactions to the
analogous 1-phenyl-3-methyl compound, is, however, not hydrolysed on
boiling with alcoholic potassium hydroxide ; it gives a deep green
copper derivative, m. p. 245—246° (decomp.) ; the *phenylhydrazone* as
first obtained from reaction in chloroform or alcohol forms colourless
needles, m. p. 208—209°, but on recrystallisation from alcohol passes
into yellow, prismatic needles of an isomeride, m. p. 204—205°, which
is directly produced in benzene solution.

1-*p*-Tolyl-3-methylpyrazolone, prepared from *p*-tolylhydrazine and
ethyl acetoacetate, undergoes condensation with ethyl oxalate under
the previous conditions, yielding yellow needles of the *potassium*
derivative of *ethyl 1-p-tolyl-3-methyl-5-pyrazolone-4-glyoxylate* ; this
ester, which forms yellow needles, m. p. 87—88°, gives a deep red
coloration with alcoholic ferric chloride, and a red changing to violet
with common benzene and sulphuric acid.

1-p-*Tolyl-3-methyl-5-pyrazolone*-4 - *glyoxylic acid* forms colourless needles, m. p. 218—219°. Treatment of the ester with the calculated quantity of phenylhydrazine gives a mixture of almost colourless needles and yellow leaflets. The former, purified by recrystallisation from alcohol, have m. p. 195—196°, whilst the latter, m. p. 209—210°, are obtained pure by crystallisation from warm chloroform ; these two *phenylhydrazones* are isomeric, the structures :

$$\begin{array}{c}NPh\cdot CO\\ \diagdown\\ N=CMe\end{array}\!\!\!\!>CH\cdot C(:N\cdot NHPh)\cdot CO_2Et \quad \text{and}$$

$$\begin{array}{c}NPh\cdot CO\\ \diagdown\\ N=CMe\end{array}\!\!\!\!>C:C(\cdot NH\cdot NHPh)\cdot CO_2Et$$
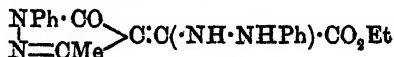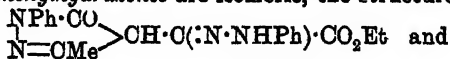
being suggested for the colourless and yellow forms respectively. A similar explanation is proposed for the occurrence of the other isomeric phenylhydrazones described above.

Tolylmethylpyrazoloneglyoxylic acid with phenylhydrazine in benzene solution first gives colourless needles, m. p. 201—202°, of a *phenyl-hydrazine* salt, which loses a molecule of water on recrystallisation from hot alcohol, producing the *phenylhydrazone*, yellow leaflets, m. p. 217°. No isomerism was observed with this phenylhydrazone or with the *diphenylhydrazone* of ethyl tolylmethylpyrazoloneglyoxylate, prisms, m. p. 137—138°.   D. F. T.

Preparation of *N*-Halogenalkyl-5 : 5-dialkylbarbituric Acids. E. MERCK (D.R.-P. 265726).—*N*-Halogenalkyl-5 : 5-dialkylbarbituric acids of general formula $CRR_1\!\!<\!\!\begin{array}{c}CO\cdot NX\\ CO\cdot NY\end{array}\!\!>\!CO$ (where R and R_1 are alkyl, X halogenalkyl, and Y hydrogen or halogenalkyl groups) are obtained when *N*-alkylen-5 : 5-dialkylbarbituric acids are treated with the required halogen, or when dialkylmalonyl haloids are combined with halogenated alkylcarbamides.

5 : 5-*Diethyl*-1-*allylbarbituric acid* forms colourless needles, m. p. 77° ; and when treated (in cooled acetic acid solution) with bromine, gives rise to 5 : 5-*diethyl*-1-*βγ-dibromopropylbarbituric acid*,

$$CO\!\!<\!\!\begin{array}{c}CEt_2\cdot CO\\ NH-CO\end{array}\!\!>\!N\cdot CH_2\cdot CHBr\cdot CH_2Br,$$
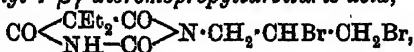
colourless needles, m. p. 126° (corr.) ; the latter compound can also be prepared by heating βγ-dibromopropylcarbamide,

$$CH_2Br\cdot CHBr\cdot CH_2\cdot NH\cdot CO\cdot NH_2,$$
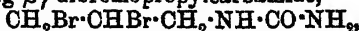
with diethylmalonyl chloride during fifteen to twenty hours at 120°.

5 : 5-*Dibenzyl*-1: *γ-bromopropylbarbituric acid*, small, hard prisms, m. p. 111°, is obtained in a similar manner from 5 : 5-dibenzyl-1-allyl-barbituric acid.

5 : 5-*Diethyl*-1-*βγ-dichloropropylbarbituric acid* has m. p. 127°, and 5 : 5-*diethyl*-1 : *γ-bromopropylbarbituric acid*, m. p. 100°.

When 5-*phenyl*-5-*ethyl*-1-*allylbarbituric acid*, m. p. 68—69° (prepared from allylcarbamide and phenylethylmalonyl ester) is treated with bromine it gives rise to 5-*phenyl*-5-*ethyl*-1-*βγ-dibromopropyl-barbituric acid*, $C_{15}H_{16}O_3N_2Br_2$, whilst 5 : 5-*diethyl*-*βγβ'γ'-tetrabromo*-1 : 1-*dipropylbarbituric acid*, $C_{14}H_{20}O_3N_2Br_4$, colourless prisms, m. p. 64°, is obtained by brominating 5 : 5-diethyl-1 : 1-diallylbarbituric acid

or by brominating *s*-diallylcarbamide and heating the *tetrabromodipropylcarbamide* with diethylmalonyl chloride at 120—130° for twenty-five hours in a vacuum.   F. M. G. M.

Products of Decomposition of Indigo in the Vat. HERBERT EHRHARDT (*J. Soc. Dyers*, 1913, **29**, 321—322).—The loss of dye which is often experienced when indigo vats are reduced, not by pure solutions of sodium hyposulphite, but by metallic reducing agents, is traced to the formation of anthranilic acid. A vat containing 200 grams of pure 20% indigo-paste, 120 grams of lime slaked with 600 c.c. of water, 200 c.c. of sodium hydrogen sulphite solution of 57° Tw., and 30 grams of zinc was left for a few days. The sediment was then filtered and extracted with boiling water, whilst the solution was oxidised by a current of air and the precipitated indigo extracted with dilute hydrochloric acid. The combined solutions were then cooled, roughly titrated with sodium nitrite, and treated with the requisite amount of β-naphthol, when 2 grams of the azo-dye of anthranilic acid were obtained.   J. C. W.

Formation of Pyrazine Compounds from Quinoxaline Derivatives. K. A. BÖTTCHER (*Ber.*, 1913, **46**, 3084—3087. Compare Gabriel and Sonn, A., 1908, i, 60).—2-*Methylquinoxaline*,

$$C_6H_4\left<{\overset{N\colon CMe}{N\colon CH}}\right>,$$
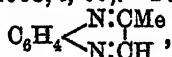
b. p. 245—247°, is formed by the condensation of *o*-phenylenediamine with oximinoacetone in aqueous acetic acid solution. It solidifies in a freezing mixture of ice and salt, and is rapidly discoloured on exposure to sunlight. The *platinichloride*, unstable, yellow needles, darkens at 130°, and is not melted at 250°, whilst the *gold* salt softens at 122° and has m. p. 135° (decomp.). The *picrate* blackens below 200° and has m. p. 215°. Oxidation with alkaline permanganate converts 2-methylquinoxaline into 2-*methylpyrazine*-5 : 6-*dicarboxylic acid*,

$$\overset{CMe\colon N\colon C\cdot CO_2H}{\underset{CH-N\colon C\cdot CO_2H}{}}$$
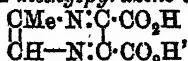
which, after purification through the *calcium* and *barium* salts, has m. p. 196°. The *copper* salt, $C_7H_4O_4N_2Cu, H_2O$, pale blue needles which decompose below the m. p., and the *silver* salt, $C_7H_4O_4N_2Ag_2$, were analysed.

2 : 3-Dimethylquinoxaline (compare Gabriel and Sonn, *loc. cit.*) crystallises with $2H_2O$. 2 : 3-Dimethylpyrazine-5 : 6-dicarboxylic acid, after purification by means of the barium salt, has m. p. 190°, instead of 200° as previously recorded. When treated with methyl alcohol and hydrogen chloride, it yields an oily *methyl* ester, which is also prepared by the action of methyl iodide on the silver salt. The *diamide*, needles, m. p. 227°, is obtained by the action of methyl alcoholic ammonia on the ester.   H. W.

Indigoid Derivatives of Phenyl*iso*oxazolone. ANDRÉ MEYER (*Bull. Soc. chim.*, 1913, [iv], **13**, 992—1000).—The author has prepared a number of indigoid derivatives from phenyl*iso*oxazolone or its substituted derivatives as follows. Phenyl*iso*oxazole-2-indole,

prepared by heating indoxylic acid with dibromophenyl*isooxazolone* in acetic acid in the presence of sodium acetate, crystallises from glacial acetic acid in red needles (compare Wahl, A., 1909, i, 261). In order to study the effect of substitution on the colour and properties of this indigoid dye, the author has prepared the following derivatives by the condensation of substituted isatin chlorides with phenyl*isooxazolone*, which gives substances with the general constitution (annexed formula).
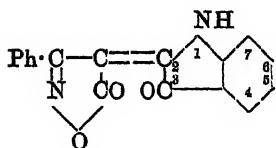
*Phenyl*isooxazole-5-*bromo*-2-*indole* crystallises from acetic acid in deep, reddish-brown needles, its properties being closely allied to those of the non-halogenated indigoid dye.

*Phenyl*isooxazole-5 : 7-*dibromo*-2-*indole* crystallises in red plates, its colour being brighter and its solubility in organic solvents much greater than that of the two preceding compounds.

*Phenyl*isooxazole-2-*nitroindole*, scarlet-red needles, m. p. 220°, gives an eosin-red solution in concentrated sulphuric acid.

β-Naphthisatin chloride reacts similarly with phenyl*isooxazolone*, giving *phenyl*isooxazole-2-β-*naphthindole*, crystallising from ethylene bromide in brown needles.

Oxythionaphthen reacts with dibromophenyl*isooxazolone* in acetic acid solution, yielding *phenyl*isooxazole-2-*thionaphthen*, crystallising in scarlet red needles, giving a greenish coloration with sulphuric acid and a deep red precipitate from benzene solution with stannic chloride.
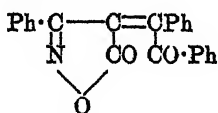
Phenyl*isooxazolone*, unlike other heterocyclic compounds, such as indoxyl and oxythionaphthen, does not condense with cyclic ketones to give any well-defined products, but with benzil in alcoholic solution in the presence of piperidine the author has succeeded in preparing *phenyl*isooxazoledibenzil (annexed [formula), yellow needles, m. p. 208°. W. G.

3 : 6-Diaminoacridine. Relationships between Acridine Derivatives and Analogous Phenazine Compounds. EUGÈNE GRANDMOUGIN and K. SMIROUS (*Ber.*, 1913, 46, 3425—3434).—In view of the similarity in the structure of 3 : 6-diaminoacridine (Benda, A., 1912, i, 651) and 3 : 6-diaminophenazine, the authors have undertaken a comparison of the behaviour of these two compounds and their derivatives, the present paper dealing particularly with the salt-formation and diazotisation of the first-mentioned compound. The salts of 3 : 6-diaminoacridine with one equivalent of acid are quite stable, whilst those with two or three equivalents are readily hydrolysed by water.

Addition of alkali to a concentrated solution of 3 : 6-diamino-10-methylacridinium chloride (trypaflavine of Ehrlich and Benda this vol., i, 904) precipitates the orange-yellow *imine base*,

$$NH_2 \cdot C_6H_3 \underset{NMe}{\overset{CH}{<}}{>} C_6H_3 \cdot NH;$$
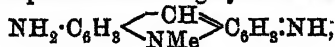
ethereal solutions of which, when shaken with water, yield the *ammonium base*, $NH_2 \cdot C_6H_3 \underset{NMe(OH)}{\overset{OH}{<}} C_6H_3 \cdot NH_2$, the latter being converted by heating with water into the *carbinol base*,

$$NH_2 \cdot C_6H_3 \underset{NMe}{\overset{OH(OH)}{<}} C_6H_3 \cdot NH_2.$$
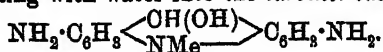
On diazotisation, 3 : 6-diaminoacridine yields a violet monodiazo-compound, which on account of its colour is considered to have a *p*-quinonoid structure : $NH \overset{..}{:} C_6H_3 \underset{NH}{\overset{CH}{<}} C_6H_3 \cdot N_2Cl.$

The diazo-compound combines with resorcinol, β-naphthol, and R-salt to form reddish-brown to reddish-violet *azo-dyes*, and is reduced by alcohol to 3-*aminoacridine*, m. p. 170°, which is orange-yellow in colour, yields yellow aqueous solution having a green fluorescence, and can be further diazotised and reduced to acridine.

On treatment with potassium iodide, the monodiazo-compound yields 3-*iodo*-6-*aminoacridine*, orange crystals, m. p. 230° (decomp.).

Diazotisation with excess of sodium nitrite in concentrated sulphuric acid solution yields a bisdiazo-compound, which, with potassium iodide, gives rise to 3 : 6-*di-iodoacridine*. This forms dark brown crystals of a metallic lustre, m. p. 270° (decomp.), and, when methylated by means of methyl sulphate in nitrobenzene solution and subsequently treated with potassium iodide, is converted into an orange-yellow, crystalline 3 : 6-*di-iodo*-10-*methylacridinium iodide*.

The *dihydrochloride* of 3 : 6-diaminoacridine, prepared by the addition of concentrated hydrochloric acid to an alcoholic solution of the monohydrochloride, crystallises in orange-yellow needles.

The *trihydrobromide*, obtained from the free base and alcoholic hydrogen bromide, forms orange crystals. The *monohydrochloride* of 3 : 6-diacetylaminoacridine forms slender, yellow crystals.

3 : 6-*Diamino*-10-*methylacridinium dihydrochloride*, prepared by the action of methyl sulphate on 3 : 6-diacetylaminoacridine in nitrobenzene solution, and subsequent hydrolysis of the resulting brownish-yellow *methosulphate* by means of hydrochloric acid, forms dark brownish-red crystals of a metallic lustre, and when warmed readily loses hydrogen chloride with the formation of the monohydrochloride.

3 : 6-*Diamino*-10-*methylacridinium bromide* forms Bordeaux-red leaflets of a metallic lustre, the *iodide*, orange needles, and the *nitrate*, reddish-brown needles.

The diazotisation of safranine has also been studied. According to Kehrmann, Havas, and Grandmougin (this vol., i, 1241), the green safranine salts formed by the combination of one molecule of the base with three equivalents of acid, consist of a mixture of the yellow *o*-quinonoid salt I and the blue *p*-quinonoid salt II :

(I.) $NH_3X \cdot C_6H_3 \underset{NPhX}{\overset{N}{<}} C_6H_3 \cdot NH_3X$

(II.) $NH_3X \cdot C_6H_3 \underset{NPhX}{\overset{N}{<}} C_6H_3 \overset{..}{:} NH,HX.$
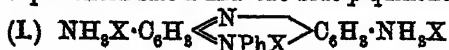
Of these two salts only the *o*-quinonoid form should be capable of complete diazotisation.

This view has been confirmed by the behaviour of phenosafranine, which on treatment with solid sodium nitrite in concentrated sulphuric acid solution is partly converted into a bisdiazo-compound. If the solution is kept, the p-quinonoid salt II is slowly transformed into the o-quinonoid form and then undergoes complete diazotisation.

Reduction of the resulting solution by means of alcohol yields the phenylphenazonium of Kehrmann (A., 1897, i, 107). F. B.

The Degradation of Allantoin to Hydroxonic Acid, and a New Synthesis of Allantoin. HEINRICH BILTZ and ERHARD GIESLER (*Ber.*, 1913, **46**, 3410—3425).—Allantoin, prepared from uric acid by oxidation with alkaline potassium permanganate solution, was further oxidised to potassium allantoxanate; by treating this in aqueous solution with slightly less than the calculated amount of N-sulphuric acid, more than 90% of the theoretical quantity of allantoxaidin (from decomposition of the unisolable allantoxanic acid,

$$\begin{array}{c} CO\cdot NH \\ \diagdown \\ NH-CO \end{array}>C\overset{..}{:}N\cdot CO_2H),$$
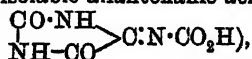
was obtainable (compare Ponomarev, A., 1879, 226, 228, 461); the allantoxaidin, $CO<\begin{smallmatrix}NH\cdot C:NH\\NH\cdot CO\end{smallmatrix}$, was obtained in short prisms containing $1H_2O$, and of m. p. 282° (decomp.); its aqueous solution on heating yields biuret and formic acid, and a similar decomposition ensues on heating the substance with acetic anhydride, the product being *formylacetylbiuret*, probably $CHO\cdot NH\cdot CO\cdot NH\cdot CO\cdot NHAc$, leaflets, m. p. 184—185°.

The reduction of potassium allantoxanate by sodium amalgam and water (compare Ponomarev, *loc. cit.*) gave rise to the product described by Ponomarev as hydroxonic acid, $C_8H_{10}O_7N_6$, but when this was purified by means of the ester, it was found to be of the composition $C_4H_5O_4N_3$, that is, *dihydroallantoxanic acid*,

$$\begin{array}{c} CO\cdot NH \\ \diagdown \\ NH-CO \end{array}>CH\cdot NH\cdot CO_2H;$$
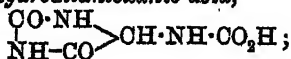
potassium salt, rectangular prisms, rapid decomp. near 333°; *ammonium* salt, colourless needles, unfused even at 340; *silver* salt with $1H_2O$; *methyl* ester, leaflets, m. p. 275° (decomp.); *ethyl* ester, rectangular tablets, m. p. 277° (decomp.).

The above results indicate that allantoin is the amide of dihydroallantoxanic acid, but it was not found possible to convert the esters of the latter substance into allantoin, nor was it possible to obtain allantoxanic acid directly from allantoin, but the existence of the relationship could be demonstrated in the following manner.

When hydroxonic acid is boiled with acetic anhydride for eight hours, it undergoes loss of carbon dioxide with formation of $1:3:6$-*tri-acetyl-5-aminohydantoin*, $\begin{array}{c} CO\cdot NAc \\ \diagdown \\ NAc-CO \end{array}>CH\cdot NHAc$, tablets from acetone or prisms from benzene, m. p. 184—185°; this substance when boiled with alcohol gives leaflets, m. p. 240—241°, of $1:6$-*diacetyl-5-amino-hydantoin*, which on evaporation with concentrated hydrochloric acid is converted into *5-aminohydantoin hydrochloride*, m. p. 218—222°

(decomp.); the free base, of which the *platinichloride* was also prepared, could not be isolated; the action of silver oxide on the hydrochloride produced insoluble 3-*silver*-5-*aminohydantoin*. Allantoin itself was obtainable from the hydrochloride of the aminohydantoin by treatment with potassium cyanate in aqueous solution.   D. F. T.

Ring Formation between the Nitro- and Amino-groups with Production of Triazines. FRITZ ARNDT (*Ber.*, 1913, **46**, 3522—3530).—The preparation and properties of a number of triazines are described which are obtained from o-*nitrophenylguanidine* and o-nitrophenylcarbamide by loss of water under the influence of sodium or potassium hydroxide. Since neither sodium carbonate, ammonia nor acids bring about this change, it seems probable that ring formation is preceded by formation of the alkali salt of the ψ-nitro-form. This is the more likely, since the originally orange-yellow solution becomes red when warmed with alkali, and then yields a yellow precipitate. After ring formation, the reverse change immediately occurs, since the product obtained does not possess the properties of an o-quinone.

If Angeli's formula for the azoxy-group (this vol., i, 658) is adopted, the compounds obtained by the author may be regarded as containing this group in the triazine ring, and it therefore seems to be produced with remarkable ease by loss of water from an amino- and nitro-group, when ring formation can simultaneously occur.

o-*Nitrophenylguanidine nitrate*, pale yellow prisms, m. p. 160°, is obtained by the addition of 2N-nitric acid to the product of the action of concentrated hydrochloric acid on a mixture of o-nitroaniline and cyanamide. Should the latter contain dicyanamide, the white, amorphous *nitrate* of a condensation product of cyanamide and dicyanamide is also formed. o-Nitrophenylguanidine,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot C(:NH) \cdot NH_2,$$
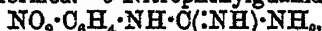
separates as a viscous oil when the finely powdered nitrate is treated with cold 2N-sodium hydroxide. It separates from its aqueous solution in orange-yellow needles which contain 1H_2O, m. p. 53°.

Aminophenotriazoxine [3-*amino*-1 : 2 : 4-*benzotriazine* 1-*oxide*] (annexed formula), shining leaflets, m. p. 269°, is obtained in almost quantitative yield by the action of boiling sodium hydroxide solution on o-nitrophenylguanidine or on the crude reaction mixture obtained
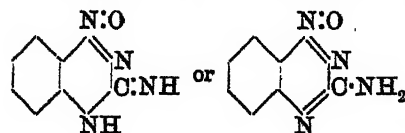
from o-nitroaniline, cyanamide and hydrochloric acid. The *hydrochloride*, *sulphate*, and *nitrate* were examined. The *silver* salt, $C_7H_5ON_4Ag$, was analysed.

Sodium nitrite and hydrochloric acid convert 3-amino-1 : 2 : 4-benzotriazine oxide directly into 3-*hydroxy*-1:2:4-*benzotriazine* 1-*oxide*, yellow leaflets, m. p. 219° (decomp.).

Aminobenzotriazine oxide is readily reduced by tin and hydrochloric acid; when 2N-nitric acid is added to the reaction product, 3-*amino*-

dihydro-1:2:4-*benzotriazine nitrate*, m. p. 195—197°
(decomp.), is obtained. When an aqueous solution
of this salt is treated with sodium carbonate, the
free *base* (annexed formula) separates in white
leaflets which rapidly become oxidised with forma-
tion of 3-*amino*-1:2:4-*benzotriazine*, yellow needles,
m. p. 207°. The latter substance is best obtained
by the action of potassium ferricyanide and sodium hydroxide on a
solution of dihydroaminophentriazine nitrate.
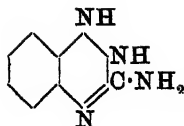
For the preparation of *o-nitrophenylcyanamide*, $NO_2 \cdot C_6H_4 \cdot NH \cdot CN$,
an intimate mixture of *o*-nitroaniline hydrochloride and lead thio-
cyanate is allowed to remain at the ordinary temperature until a
portion does not melt when placed in boiling water ; the mixture is
then heated for six to seven hours on the water-bath, and subsequently
boiled with $2N$-sodium hydroxide ; after removal of lead sulphide,
the solution is cooled, filtered from unchanged *o*-nitroaniline, and
cautiously acidified with hydrochloric acid, when *o*-nitrophenyl-
cyanamide, pale yellow needles, m. p. 152°, separates in poor yield.
Boiling dilute hydrochloric acid transforms it into *o*-nitrophenyl-
carbamide, yellow needles, m. p. 183—184° (Schwartz [A., 1897, i,
411] gives 181°), which is converted by boiling potassium hydroxide
into hydroxybenzotriazine oxide, identical with the product obtained
from aminobenzotriazine oxide.

Attempts to prepare *o*-nitrophenylthiocarbamide were unsuccessful.
H. W.

**A Mode of Decomposition of Halogenated Alkyl Deriv-
atives of Hexamethylenetetramine.** MARCEL SOMMELET (*Compt.
rend.*, 1913, **157**, 852—854. Compare Hock, A., 1903, i, 465).—
Derivatives of hexamethylenetetramine of the type $C_6H_{12}N_4RX$,
where R is an alkyl group and X one of the halogens, are decomposed
by boiling with water. This is particularly true of the derivative
obtained from benzyl chloride, the products of the decomposition being
benzaldehyde (70—80% yield) and a mixture of bases of which the
following were characterised : ammonia, methylamine, dimethylamine,
trimethylamine, and benzylamine. Benzaldehyde is similarly obtained
by boiling benzyl chloride and hexamethylenetetramine together in
aqueous alcoholic solution.

The three xylyl bromides combine directly with hexamethylene-
tetramine in chloroform solution to give the additive *compounds*,
$C_6H_{12}N_4Br \cdot CH_2 \cdot C_6H_4Me$, having melting points respectively,
ortho, 198°; *meta*, 215°; *para*, 216°. Each of these are similarly
decomposed by boiling with water, giving the corresponding
tolualdehydes.

The course of this decomposition reaction is not yet clear, but the
relatively abundant production of methylamine points to the possible
primary production of benzylmethyleneamine, which undergoes
isomerisation to benzylidenemethylamine :
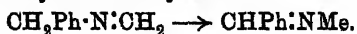
$$CH_2Ph \cdot N:CH_2 \longrightarrow CHPh:NMe. \qquad W. G.$$

Anilinoquinones and their Azine Derivatives.   FRIEDRICH KEHRMANN and MARCELIEN CORDONE (*Ber.*, 1913, **46**, 3009—3014).— The authors have convinced themselves of the correctness of Will-stätter's view as to the holoquinonoid nature of both modifications of *o*-benzoquinone, but believe that these merely represent dimorphous forms of the same substance.   *o*-Benzoquinone is said to present an example of dichroism, on account of which the different crystalline forms appear to be of different colours; the less stable form is stated to be not colourless but green.   Both forms of the substance are, therefore, of diketonic structure.

If catechol is oxidised in the presence of aniline by silver acetate in solution in cold acetic acid, a brown mixture of 4 : 5-*dianilino-o-benzo-quinone* (annexed formula), brownish-red needles, m. p. 193°, with a little of the trianilino-compound separates; the former is easily extracted by sodium hydroxide, in which it is soluble.

$$\text{NHPh}$$
$$\text{NHPh} \diagup \diagup \diagdown \text{:O}$$
$$\dot{\text{O}}$$
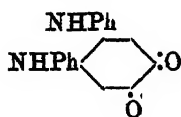
When equimolecular quantities of the above dianilinobenzoquinone and *o*-phenylenediamine hydrochloride are heated together in concentrated solution in alcohol, condensation occurs to 2 : 3-*dianilinophenazine*,

$$\text{C}_6\text{H}_2(\text{NHPh})_2 \diagdown^{\text{N}}_{\text{N}} \diagup \text{C}_6\text{H}_4,$$
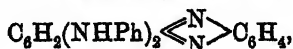
orange-yellow, apparently rhombohedral crystals, m. p. 218—219°, which separate from alcohol with one $\text{C}_2\text{H}_6\text{O}$; the *hydrochloride*, which is the primary product, forms long, deep red needles.

A similar condensation could be effected between the dianilino-*o*-benzoquinone and phenyl-*o*-phenylenediamine hydrochloride, the product being 2 : 3-dianilino-10-phenylphenazonium chloride,

$$\text{C}_6\text{H}_2(\text{NHPh})_2 \diagdown^{\text{N}\text{------}}_{\text{NPhCl}} \diagup \text{C}_6\text{H}_4,$$

violet tablets, m. p. 235—237° (compare Fischer and Hepp, A., 1896, i, 50).

Under similar conditions to the above, 3-anilino-4-hydroxy-*o*-benzoquinone (Zincke, A., 1885, 787) condenses with *o*-phenylenediamine hydrochloride; producing long, deep red needles of the *hydrochloride* of 2-*anilino-3-hydroxyphenazine*; the free base forms brownish-red needles, decomp. above 200°.   Condensation with phenyl-*o*-diphenylenediamine gave rise to two products which are probably 3-anilino-2-hydroxy-10-phenylphenazonium chloride and 2-anilino*aposafranone*,

$$\text{C}_6\text{H}_4 \diagdown^{\text{------N}}_{\text{NPh}} \diagup \text{C}_6\text{H}_2(\text{NHPh})\text{O},$$

The constitution of the above dianilino-*o*-benzoquinone is demon-strated by hydrolysis with dilute solutions of alkali, which gives rise to the *s*-dihydroxyquinone of Nietzki and Schmidt (A., 1888, 1181). Of the three possible isomerides having the composition of a dianilino-quinone, two are already known, so that to this third isomeride is to be ascribed the remaining structure, 4 : 5-dianilino-*o*-benzoquinone.

                                        D. F. T.

Purines. XII. Carl O. Johns and Emil J. Baumann (*J. Biol. Chem.*, 1913, **15**, 515—521. Compare this vol., i, 774, 1000).— 5-Amino-6-ethylamino-2-hydroxy-4-methylpyrimidine reacts smoothly with the reagents commonly used for the preparation of purines. Thus, when the formyl derivative is heated, 2-*oxy-6-methyl-9-ethyl-purine*,

$$\begin{matrix} N:CMe \cdot C—N \\ CO \cdot NH \cdot C \cdot NEt \end{matrix}\!\!>\!CH,$$

is formed. This crystallises in a net work of silky needles, which begin to melt at 256°, m. p. 275° (decomp.).

Similarly, the corresponding acetyl derivative yields 2-*oxy-6 : 8-dimethyl-9-ethylpurine*, which also forms a network of silky needles, m. p. 265° (decomp.) to a dark oil.

2-*Oxy-8-thio-6-methyl-9-ethylpurine* is formed when the diamino-pyrimidine is heated with thiocarbamide; it crystallises in colourless sheaves, decomp. 295—300°. When the components are mixed in hot water, a thiocarbamide additive product of the pyrimidine is obtained; this has m. p. 204—206° (decomp.), and gives the thiopurine when heated.

The thiopurine reacts with monochloroacetic acid, forming 2-*oxy-6-methyl-9-ethylpurine-8-thiolacetic acid*,

$$\begin{matrix} N:CMe \cdot C—N \\ CO \cdot NH \cdot C \cdot NEt \end{matrix}\!\!>\!CS \cdot CH_2 \cdot CO_2H.$$
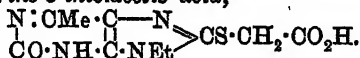
This separates as a bulky mass of needles, which darken at 270°. It is stable in hot water, but boiling with concentrated hydrochloric acid hydrolyses it to 2 : 8-dioxy-6-methyl-9-ethylpurine.

The action of thiophosphoryl chloride on 4 : 5-diamino-6-hydroxy-2-methylthiolpyrimidine converts it into 6-*oxy-8-thio-2-methylthiolpurine*,

$$\begin{matrix} NH \cdot CO \cdot C \cdot NH \\ SMe \cdot C—N—C \cdot NH \end{matrix}\!\!>\!CS.$$

This separates in small globules, which begin to decompose at 275°, and give the murexide test. E. F. A.

Purines. XIII. 2 : 8-Dioxy-1 : 6-dimethyl-1 : 2 : 8 : 9-tetra-hydropurine and 5-Nitro-3 : 4-dimethyl-1 : 2 : 3 : 6-tetrahydro-pyrimid-2 : 6-dione (α-Nitrodimethyluracil). Carl O. Johns and Emil J. Baumann (*J. Biol. Chem.*, 1913, **16**, 135—142).—Methyl sulphate and an aqueous solution of the sodium salt of 5-nitro-6-amino-4-methyl-2 : 3-dihydro-2-pyrimidone react at the ordinary temperature to form, in 80% yield, 5-*nitro-6-amino-3 : 4-dimethyl-2 : 3 - dihydro-2-pyrimidone*,

$$CO\!\!<\!\!\begin{matrix} N:C(NH_2) \\ NMe \cdot CMe \end{matrix}\!\!>\!C \cdot NO_2,$$

decomp. 170—195°, prisms containing $\frac{1}{2}H_2O$. The position of the new methyl group is established as follows. By heating with 25% sulphuric acid at 160°, the substance is converted into 5-*nitro-3 : 4-dimethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione*,

$$CO\!\!<\!\!\begin{matrix} NH—CO \\ NMe \cdot CMe \end{matrix}\!\!>\!C \cdot NO_2,$$

m. p. 191°, slender prisms (the only other possible 5-nitrodimethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione is Lehmann's 5-nitro-1 : 4-dimethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione, m. p. 149°), which is oxidised by nitric acid, D 1·5, and concentrated sulphuric acid on the water-bath to 5-nitro-3-methyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione-4-carboxylic acid, which cannot be

isolated, since it loses carbon dioxide and changes to Behrend's 5-nitro-3-methyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione, m. p. 255°.

The reduction of 5-nitro-6-amino-3 : 4-dimethyl-2 : 3-dihydro-2-pyrimidone by aqueous ammonia and ferrous sulphate produces 5 : 6-*diamino-3 : 4-dimethyl-2 : 3-dihydro-2-pyrimidone*, $C_6H_{10}ON_4$, decomp. about 230°, colourless plates, in 40% yield ; the latter and an equal weight of carbamide at 170—180° produce 2 : 8-*dioxy-1 : 6-dimethyl-1 : 2 : 8 : 9-tetrahydropurine*,

$$\begin{array}{c} \text{NMe·CMe:C·NH} \\ \vert \qquad\qquad\qquad \rangle\text{CO, decomp. 260—265°,} \\ \text{CO—N=C·NH} \end{array}$$

prisms containing H_2O ; by evaporating the latter with nitric acid and treating the yellow residue with an alkali, a rose coloration is developed.   C. S.

Bistetrazole and Isomeric Derivatives of Tetrazole. E. OLIVERI-MANDALÀ and T. PASSALACQUA (*Gazzetta*, 1913, **43**, ii, 465—474. Compare A., 1912, i, 144).—When cyanotetrazole (*loc. cit.*) is further acted on with azoimide, or when cyanogen is passed into an aqueous solution of azoimide as in the experiment formerly described, but using a more concentrated solution, bistetrazole and the amide of tetrazolecarboxylic acid are produced in addition to cyanotetrazole, which still forms the chief product of the reaction. Saponification of the cyanotetrazole yields (by way of the unstable carboxylic acid) tetrazole, and this is the best way of preparing this substance. The preparation is conveniently carried out by heating the sodium salt described below with hydrochloric acid, evaporating to dryness, and extracting the tetrazole with warm acetone. *Bistetrazole* (annexed formula) forms prismatic crystals, m. p. 254—255° (decomp.). Bistetrazole and especially its *silver* salt are explosive. The substance has about the calculated molecular weight in freezing water. The *barium* salt, $C_2N_8Ba,3H_2O$, was prepared. Bistetrazole is decomposed by warm, concentrated sulphuric acid according to equation : $C_2H_2N_8 + 2H_2O + O_2 = 3N_2 + 2CO_2 + 2NH_3$, so that the sulphuric acid acts as an oxidiser.
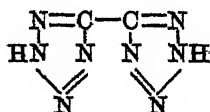
$$\begin{array}{c} \text{N=C—C=N} \\ \vert \quad\; \vert \quad\; \vert \quad\; \vert \\ \text{HN} \;\; \text{N} \;\;\; \text{N} \;\; \text{NH} \\ \diagdown\!\diagup \quad \diagdown\!\diagup \\ \text{N} \qquad\; \text{N} \end{array}$$

The above-mentioned *tetrazole-5-carboxylamide*, $C_2H_3ON_5$, has m. p. 234° (decomp.). *Sodium 2-sodiotetrazole-5-carboxylate*, $C_2O_2N_4Na_2$, is obtained by saponification of the amide or of the cyanotetrazole. The *barium* salt has the composition $C_2N_4O_2Ba,3\frac{1}{2}H_2O$.

5-Cyano-2-methyltetrazole, $C_3H_3N_5$, b. p. 100—102°/16 mm., is obtained by boiling the silver salt of 5-cyanotetrazole with an ethereal solution of methyl iodide. When it is saponified with alcoholic sodium hydroxide, the *sodium* salt of the corresponding acid, $C_3H_3O_2N_4Na$, is produced, and from this the free 2-*methyltetrazole-5-carboxylic acid*, $C_3H_4O_2N_4$ (prisms, m. p. 204—205°, losing CO_2), can be prepared. When this acid is heated at its m. p., 2-*methyltetrazole*, $C_2H_4N_4$, b. p. 145—147°/759 mm., is obtained.

When the silver salt of tetrazole and ethyl iodide are heated in benzene solution for some hours, 2-ethyltetrazole and 1-ethyltetrazole are produced. 2-*Ethyltetrazole*, $C_3H_6N_4$, has b. p. 70—71°/35 mm., or

152—155° at ordinary pressure. 1-*Ethyltetrazole*, $C_3H_6N_4$, has b. p. 162—164°/30 mm. R. V. S.

The Hydrolytic Constants of Some Derivatives of Tetrazole. E. OLIVERI-MANDALÀ (*Gazzetta*, 1913, **43**, ii, 487—493. Compare preceding abstract).—Measurements of the catalysis of methyl acetate give the following values for the constants of hydrolysis : 2-methyltetrazole, 0·00026 ; 1-methyltetrazole, 0·000047 ; 2-ethyltetrazole, 0·00049 ; 1-ethyltetrazole, 0·00014. R. V. S.

Action of Nitrogen Peroxide on Aliphatic Diazo-compounds and on Tetrazens. HEINRICH WIELAND and CURT REISENEGGER (*Annalen*, 1913, **401**, 244—251).—Ethyl diazoacetate and nitrogen peroxide react in cold benzene to form ethyl dinitroacetate and nitrogen, ethyl furoxandicarboxylate being obtained as a by-product. Similarly, at the ordinary temperature, nitrogen peroxide and diazodeoxybenzoin yield ωω-dinitrotoluene, probably by the decomposition of the initially formed benzoyl derivative.

Nitrogen peroxide and diphenyleneazomethylene (Staudinger and Kupfer, A., 1911, i, 751) react in cold benzene in the absence of moisture to form nitrogen and 9 : 9-*dinitrofluorene*, $\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!>\!C(NO_2)_2$, m. p. 128° (decomp.), colourless needles, which yields fluorenone above its m. p.

Nitrogen peroxide and tetraphenyltetrazen in cold benzene yield a deep green solution of an additive compound, which decomposes at the ordinary temperature with the formation of pp′-*dinitrotetraphenyltetrazen*, $NO_2 \cdot C_6H_4 \cdot NPh \cdot N\!:\!N \cdot NPh \cdot C_6H_4 \cdot NO_2$, decomp. 160°, orange-yellow crystals.

The substance is proved to be a tetrazen by the liberation of nitrogen and the production of an intensely blue solution by treatment with concentrated sulphuric acid ; the positions of the nitro-groups are proved by reduction, whereby ammonia and *p*-aminodiphenylamine (2 mols.) are produced. In a similar reaction, nitrogen peroxide and diphenyldiethyltetrazen yield *di*-p-*nitrophenyldiethyltetrazen*, $C_{16}H_{18}O_4N_6$, orange-red needles, which is converted into *p*-phenylene-ethyldiamine by reduction. C. S.

The Real Nature of the So-called Artificial Globulin. HUBERT W. BYWATERS and D. G. C. TASKER (*J. Physiol.*, 1913, **47**, 149—158) —Several observers have stated that on keeping, the serum albumin in blood and urine is converted into globulin. The artificial product when analysed is found not to be identical with the natural globulin, but it is really alkaline meta-protein. W. D. H.

Colloidal Properties of Hæmoglobin. Modifications of the Viscosity and Surface Tension of Suspensions of Methæmoglobin by the Action of Hydrochloric Acid or Sodium Hydroxide. II. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 263—270).—The viscosity and surface tension of aqueous suspensions of methæmoglobin (compare this vol., i, 1249), previously

purified by dialysis for four months or longer, differ little from those of distilled water. When the methæmoglobin is brought into solution by means of hydrochloric acid or sodium hydroxide, increased viscosity and diminished surface tension are shown by the liquid, which is at first a suspension solution and finally yields a perfect solution. Continued addition of acid or alkali does not lower the surface tension beyond a certain value, which seems to be independent of the concentration of the dissolved methæmoglobin so long as this lies within certain limits; neutralisation of the acid (alkali) with an equal volume of alkali (acid) causes precipitation of the methæmoglobin and increase of the surface tension.

The increased velocity caused by hydrochloric acid diminishes considerably when excess of acid is added, and tends to return to its original value, although no precipitation occurs. This seems to be due to the influence of the acid in lowering the dissociation of the methæmoglobin chloride, and hence the concentration of the methæmoglobin ions, on which the increased viscosity depends.

Addition of sodium chloride to solution of sodium methæmoglobinate produces a further small, constant diminution in the surface tension, although the salt has no appreciable effect on a solution of pure methæmoglobin (compare Bottazzi and d'Agostino, this vol., ii, 115).

T. H. P.

Action of Quinones on Wool and Other Protein Substances. LOUIS MEUNIER (*Zeitsch. angew. Chem.*, 1913, **26**, 616).—The results described by Scharvin (this vol., i, 661) have already been published by Meunier and incorporated in certain patents (compare A., 1908, i, 586, and D.R.-P. 240512).   J. C. W.

Products of Hydrolysis of Thynnine and Percine. ALBRECHT KOSSEL and F. EDLBACHER (*Zeitsch. physiol. Chem.*, 1913, **88**, 186—189).—Thynnine yields an aminovaleric acid, proline, and tyrosine on hydrolysis. The same acids were obtained from percine. Acids of the C_5-series play the chief part in the constitution of the protamines, C_6-acids being only occasionally present. The latter play the more important part in the higher proteins.   E. F. A.

The Stability of Invertase. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **56**, 495—497).—The invertase was found to be still intact in an expressed yeast juice which had been allowed to autolyse for 470 days.   S. B. S.

Amylases. VI. A Comparison of Amyloclastic and Saccharogenic Powers. HENRY C. SHERMAN and M. D. SCHLESINGER (*J. Amer. Chem. Soc.*, 1913, **35**, 1784—1790).—In the investigation of the action of amylase on starch, the amount of reducing sugar produced is not always proportional to the amount of starch apparently digested.

The authors find that with specimens of pancreatic amylase the amount of starch apparently digested (amyloclastic power) is about twice the amount of maltose produced (saccharogenic power), whilst

with malt amylase the ratio of maltose formed to st irch apparently
digested is much higher ; indeed, with some specimens of the latter,
the amount of maltose exceeds the quantity of starch apparently
digested. The application of the starch-iodine coloration is therefore
evidently not well adapted for the measurement of the starch-digesting
power of malt amylase.   D. F. T.

**Amylases. VII. The Forms of Nitrogen in Amylase
Preparations from the Pancreas and from Malt, as Shown
by the Van Slyke Method.** HENRY C. SHERMAN and A. O.
GETTLER (*J. Amer. Chem. Soc.,*. 1913, **35**, 1790—1794).—Analysis
has been made of various specimens of pancreatic and malt amylase by
the Van Slyke method, and the results as to the nature and relative
quantity of the hydrolytic products indicate that the amylase pre-
parations used were essentially protein substances. All the eight
forms of nitrogen recognisable by the Van Slyke method were present,
the proportions being within the range of variation shown by typical
protein substances.   D. F. T.

The Partial Purification of the Esterase from Pig's Liver.
GEORGE PEIRCE (*J. Biol. Chem.*, 1913, **16**, 1—3).—Pig's liver was
ground up, strained, and water added, incubated at 37° for one day,
and, after remaining several weeks at room temperature, was filtered.
This crude enzyme solution was dialysed and filtered ; dialysis removed
about 90% of the solids, and the solution lost about 20% of its activity.
Ammonium sulphate was then added nearly to half saturation and the
liquid filtered. The precipitate was inactive. The filtrate was then
fully saturated with the same salt, and filtered ; the filtrate was inactive.
The precipitate was then dissolved in water and dialysed until free
from sulphate. This represents the most highly purified solution
obtained ; it was very active ; no attempt was made to obtain a solid
from it.   W. D. H.

**The Compound Formed between Esterase and Sodium
Fluoride.** GEORGE PEIRCE (*J. Biol. Chem.*, 1913, **16**, 5—18).—The
compound formed between esterase (from pig's liver) and sodium
fluoride has little if any action on ethyl butyrate. The formation of
this compound is reversible. When the concentration of the fluoride
is varied from 0·009 to 0·27 mg. per litre, the inhibition increases
from 20 to 88%. The inhibiting effect hardly varies at all with the
concentration of the enzyme. The conclusion is drawn that one mole-
cule of the inactive compound contains 1 molecule of enzyme and
1 molecule of sodium fluoride.   W. D. H.

The Stability of Carboxylase. CARL NEUBERG (*Biochem. Zeitsch.*,
1913, **56**, 497—498).—In a maceration juice prepared from an old
dried yeast obtained by Lebedev's method, the carboxylase was found
to be active when the zymase was no longer existent. The former
ferment appears, therefore, to be the more stable.   S. B. S.

Mercury Naphthalene Derivatives. JOHANNES GADAMER [with
R. BRIEGER and WERNER SCHULEMANN] (*Zeitsch. anyew. Chem.*, 1913,
26, 627—631).—A lecture delivered before the Verein deut. Chemiker

at Breslau. Some mercury compounds of substituted naphthalenes are discussed, and it is shown how their unusual behaviour and incoustant composition may be explained by considering the residual affinities of the atoms and groups involved.

When the sodium salt of 8-amino-1-naphthol-3 : 5-disulphonic acid (K-acid). is digested with mercuric acetate, a bright red mercuriated substance is obtained. From its method of formation and its colour, it might be expected that the mercury is attached to a carbon atom, but the fact that ammonium sulphide causes precipitation of mercuric sulphide suggests that the metal is linked with nitrogen. The colour was destroyed by the addition of alkali or sodium chloride, but was reproduced on acidifying with a mineral acid. The varying mercury-content of the product suggested that not a chemical, but rather an adsorption, compound was present, but the fact that salt or strong acetic acid decolorised solutions of the substance is not in harmony with this view.

The influence of various substituents in the naphthalene nucleus was studied, and the following conclusions are drawn : the presence of $-OH$ or $-NH_2$ in the β-position hinders the fixation of mercury, only one atom of which enters the ortho-position ; the presence of $-OH$ or $-NH_2$ in the α-position permits of the entry of two mercury atoms in the ortho- and para-positions, giving compounds which are stable towards ammonium sulphide, but tend to form unstable, coloured quinonoid compounds in the presence of reagents which reduce the acidity of their solutions ; when attempts are made to introduce more mercury into naphthol derivatives, alkali is found to remove the excess of mercury as the hydrosol of the hydroxide, but the naphthylamines can loosely fix more mercury, giving substances which are turned deep red by alkalis and decomposed by ammonium sulphide ; sulphonic acid groups render the mercury compounds more unstable.

In K-acid, the various effects indicated above are cumulative. These effects are discussed on theoretical grounds, and it is explained why these naphthalene derivatives can form compounds with indefinite quantities of mercury, in which there is no distinction between true chemical combination and adsorption.   J. C. W.

Physiological Chemistry

Water in Expired Air. WILLIAM OSBORNE (*Proc. physiol. Soc.,* 1913, xii ; *J. Physiol.,* 47).—Galeotti states that the expired air is not fully saturated with aqueous vapour, but only about three-quarters saturated. Loewy and Gerhartz point out that this is incorrect, for the temperature of expired air is not 37°, but between 32·5° and 33·5°. The present experiments confirm the latter view, and the correct theoretical figures were obtained if the

temperature is assumed to be 33·9°. The experiments were made on men in whom loss of water by the skin was prevented by a rubber suit. Such experiments are only safe in winter, as a dangerous fever may arise if the external air is too warm.

W. D. H.

Acidosis. ERNEST L. KENNAWAY, MARCUS S. PEMBREY, and EDWARD P. POULTON (*Proc. physiol. Soc.*, 1913, x—xi; *J. Physiol.*, 47).—In healthy men the value of the alveolar carbon dioxide pressure may fall below the normal (40 mm.) if carbohydrate food is withheld; in diabetes it may be normal; the determining factor is the extent of acidosis. It falls suddenly one or two days before the onset of fatal coma; a value of 25 is grave; one of 20 means that coma is imminent. Estimation of the acetone substances is not such a good guide, and suggestions are put forward to explain variations in the ratio between these substances. Their equilibrium point is probably connected with the degree of acidosis, and the high proportion of β-hydroxybutyric acid in marked cases may be due to a washing out of acetone from the blood by the increased pulmonary ventilation.

W. D. H.

The Carbon Dioxide and Oxygen Content of the Blood after Clamping the Abdominal Aorta and Inferior Vena Cava Below the Diaphragm. JOHN R. MURLIN, LEO EDELMANN, and B. KRAMER (*J. Biol. Chem.*, 1913, 16, 79—101).—The changes found are consistent with the mechanical explanation of the altered respiratory quotient after clamping the vessels. When the quotient rose, the carbon dioxide of the blood fell; when it remained stationary, the carbon dioxide did not change; when it fell, the carbon dioxide rose. Clamping off the blood from the abdominal organs therefore does not alter the character of the metabolism.

W. D. H.

The Dissociation of Carbon Dioxide from Human Blood. JOHANNE CHRISTIANSEN, CLAUDE G. DOUGLAS, and JOHN S. HALDANE (*Proc. physiol. Soc.*, 1913, ii; *J. Physiol.*, 47).—The experiments here briefly referred to show that the effect of oxygen on the carbon dioxide-carrying power of the blood is even more important than the well-known effect of carbon dioxide on its oxygen-carrying functions.

W. D. H.

The Combination of Hydrogen Arsenide in the Blood. RICHARD MEISSNER (*Chem. Zentr.*, 1913, ii. 705—706; from *Zeitsch. expt. Path. Ther.*, 1913, 13, 284—300).—The absorption capacity of the various constituents of blood for the gas was estimated by Reckleben and Lockemann's method. All solutions or suspensions were shaken for the same period with the same amount of the arsenic compound. The various lipoids in suspension or in ether and chloroform solution have practically no combining capacity in quantities in which they occur in the blood. Even the brain can combine with no more hydrogen arsenide than can physiological

saline in which it is suspended. Of the other constituents, hæmatin possesses a marked combining capacity, and blood containing carbon monoxide is less liable to hæmolysis by the arsenic compound than normal blood. The combining capacity of the iron-free hæmatoporphyrin is much smaller than that of hæmatin. It appears that the iron plays some part in the combination of the various iron compounds investigated; only sodium nitroprusside evinced any marked combining capacity, for it yielded with hydrogen arsenide a solid substance containing both iron and arsenic. The antagonistic action of various substances to hydrogen arsenide poisoning was also investigated. Cholesterol and iodipin were without effect. Various colloidal silver and mercury preparations were also tried, but, although they combine with the arsenic compound, they were too toxic to the kidneys for *intra vitam* use. Of the other substances investigated, only cadmium chloride exhibited a high combining capacity. The *in vitro* action of the hydrogen arsenide on blood gives a product with a spectrum similar to thiomethæmoglobin.   S. B. S.

The Fermentative Properties of Blood. II. The Peptolytic Ferments of Normal Animals. LUDWIG PINCUSSOHN and HELLMUTH PETOW (*Biochem. Zeitsch*, 1913, **56**, 319—329).—In continuation of the work of Pincussohn (this vol., i, 788), many examples are given to illustrate the fact that the sera of animals are capable of degrading the peptones prepared (by sulphuric acid method) from the proteins of their own organs, but not from the organs of other animals and foreign proteins. An exception was found in the case of guinea-pig serum, and attention is called to the fact that this serum is used generally for supplying the complement in various hæmolytic systems. Guinea-pig's serum also degrades silk peptone. The serum also degrades peptones prepared from the organ proteins of closely allied species. Thus the serum from the fox also degrades peptones prepared from the organs of dogs, and dog's serum degrades peptones derived from fox tissues, but not from those of any other animals. The method may therefore be applied for determining the relationship of various species.

                                                    S. B. S.

Phosphatides of the Stromata of the Red Blood Corpuscles of Sheep and Man. M. BÜRGER and H. BEUMER (*Biochem. Zeitsch.*, 1913, **56**, 446—456).—The stromata of sheep were precipitated by carbon dioxide from the lysed blood and dried. They yielded an ethereal extract, which consisted, to the extent of 70%, of cholesterol The residue, after extraction with ether, was partly soluble in alcohol at 37°. Of the alcoholic extract, part remained insoluble after treatment with ether. This was obtained in the form of a white powder of stearin-like consistency, which swelled on treatment with water, and had m. p. 180—185°. Its analysis indicated a diaminomonophosphatide, similar in its properties to the myelins. Of the ether-soluble portion of the alcoholic extract, the greater part was precipitable by acetone, and of the acetone

precipitate, part was insoluble in hot alcohol, although soluble in ether and chloroform. This was a monophosphatide with the properties of a kephalin. The stromata of sheep's corpuscles contain therefore about 5% cholesterol and 12% phosphatides, of which about half is sphingomyelin, and kephalin is a constituent of the remainder. The blood of normal individuals and of carcinomatous individuals (drawn in the latter case from the cadaver) was examined in a similar manner to that employed in the case of sheep's blood. No essential differences in the chemical composition of the stromata of normal and cancerous individuals could be found, the ethereal extract containing 71·6 and 74% of cholesterol, and the alcoholic extracts 35 and 31% of sphingomyelin. There was isolated, in addition to kephalin, from the acetone precipitate from human blood small quantities of a phosphatide with 3·3% phosphorus and 4·33% nitrogen, which yielded a clear solution in water, but was insoluble in hot alcohol and ether.   S. B. S.

Distribution of Ions in the Blood Serum. PETER RONA and PAUL GYÖRGY (*Biochem. Zeitsch.*, 1913, **56**, 416—438).—According to Zuntz and Hamburger, part of the sodium of the serum is non-diffusible, as it is in combination with the proteins. On treatment of the serum with carbon dioxide, part of this sodium should be convertible into sodium hydrogen carbonate. If therefore, serum treated with carbon dioxide is submitted to dialysis (by the compensation method repeatedly used by Rona), the outer liquid should contain more sodium hydrogen carbonate than the dialysate of a serum which has not been so treated. This was actually found to be the case, and the results confirm the statements of Zuntz. The carbon dioxide should, however, convert the serum proteins into a carbamic acid derivative. There would therefore exist in the dialysor sodium salt of a non-diffusible acid. Attention is called to the fact that, according to Donnan's theory (A., 1911, ii, 848), arrived at by thermodynamic considerations, the amount of sodium hydrogen carbonate on both sides of the dialysing membrane will not be the same when equilibrium is established, for on one side there is an electrolytically dissociated substance with a non-dialysable ion. The sodium hydrogen carbonate in the dialysor could not be estimated in a satisfactory manner by incineration. The contents were therefore submitted to ultra-filtration in a Bechhold apparatus, and the filtrate was analysed. The distribution of the chlorine was also investigated, when the [H·] concentration of the serum was altered by the addition of acetic acid. In concentration above $H\cdot = 10^{-5}$, equilibrium exists with a higher concentration of chlorine inside than outside the membrane, whereas in lower [H·] concentrations the reverse is the case. The critical point of change is the isoelectric point, through which the protein changes from the anionic to the cationic state. The Donnan theory is also applicable in this case to the determination of the distribution of the chlorine.   S. B. S.

Salts in the Coagulation of Blood. C. GESSARD (*Compt. rend.*, 1913, **157**, 799—802).—A study of the influence of various salts

on the blood of a horse. The amount of salt necessary to prevent coagulation varied with the salt employed, and the plasma obtained could be made to coagulate according to the kind and amount of salt used either by dilution or by addition of a calcium salt, or by addition of serum. Magnesium chloride and sulphate are the most appropriate for the study of these phenomena, since they do not precipitate calcium salts, give no apparent reaction with the saline constituents of blood, and for small differences in weight give different types of plasma.   W. G.

The Inactivation of Complement by Mechanical Agitation. HANS SCHMIDT (*J. Hygiene*, 1913, **13**, 291—313).—The complement in serum is inactivated by shaking. This does not seem to be associated with the precipitation of protein, which also occurs. No explanation of the inactivation is at present forthcoming.
                                                    W. D. H.

Complement Action in Regard to Surface Tension. HANS SCHMIDT (*J. Hygiene*, 1913, **13**, 314—334).—No relationship between the surface tension and complement action of serum was found.
                                                    W. D. H.

The Rate of Elimination of Nitrogen as Influenced by Diet Factors. I. The Influence of the Texture of the Diet. LAFAYETTE B. MENDEL and ROBERT C. LEWIS (*J. Biol. Chem.*, 1913, **16**, 19—36).—A standard diet was arbitrarily selected for dogs, and a constant curve of nitrogen elimination was obtained. This shows a rise reaching a maximum in the second three hours, and then a fall to the initial level early the next day. Delay in elimination is caused by adding indigestible materials, such as mineral oil, vaselin, bone ash, paraffin, filter paper, cork, agar-agar; the effect increases in the order these are enumerated. The last four cause a higher rate of elimination in the later periods. This is attributed to a slower rate of absorption, which in its turn may be produced by (1) rapid emptying of the stomach, and a consequent early exclusion of gastric digestion; (2) the indigestible material may make the digestible material less readily accessible to digestive enzymes; or (3) the final digestion products may be adsorbed by the indigestible substances. Sand gives exceptional results; it causes more rapid elimination of nitrogen during the first six hours. This is not due to increased excretion and reabsorption of digestive juices, for in starvation it has no effect.   W. D. H.

The Rate of Elimination of Nitrogen as Influenced by Diet Factors. II. The Influence of Fats and Carbohydrates in the Diet. LAFAYETTE B. MENDEL and ROBERT C. LEWIS (*J. Biol. Chem.*, 1913, **16**, 37—53).—Carbohydrates delay the elimination of nitrogen when added to a protein meal; their effect increases in the order: starch, soluble starch, sucrose, dextrose. This may be explained by the tentative suggestion that it is due to the protein-sparing action of carbohydrates. In reference to fats, cottonseed oil delays

the elimination of nitrogen, but lard and "oleo-stearin" hasten it in the early periods. The last-named effect is, however, only due to removal of sucrose from the diet. ` W. D. H.

The Rate of Elimination of Nitrogen as Influenced by Diet Factors. III. The Influence of the Character of the Ingested Protein. LAFAYETTE B. MENDEL and ROBERT C. LEWIS (*J. Biol. Chem.*, 1913, **16**, 55—77).—Extracted meat lowers the rate of nitrogen elimination; the explanation advanced is that extracted meat contains relatively more connective tissue, and therefore is not so digestible. The curves following the ingestion of caseinogen, ovovitellin, edestin, "glidine," and gelatin show no more differences than those noted in the two meat products. Egg-white or albumin and soy bean give different curves due to rate of digestion and absorption, or, in the case of soy bean, to the presence of sucrose. Proteins do not differ materially in their rate of metabolism. The opposite findings of others are discussed. W. D. H.

The Metabolism of Infants During Starvation. ARTHUR SCHLOSSMANN and HANS MURSCHHAUSER [and, in part, KARL MATTISON] (*Biochem. Zeitsch.*, 1913, **56**, 355—415).—The authors, in confirmation of their previous investigations, show that the metabolism during starvation depends on the diet consumed in the period preceding the fast, and that the more nitrogen consumed during the period the greater is the amount of body protein decomposed during the first two or three days of starvation. Similar results were obtained in the case of infants. The breast-fed children metabolise less nitrogen than the artificially fed. There is, however, a marked difference between the metabolism of the two classes during starvation, for whereas the artificially fed children excrete less nitrogen during the period of fast than during the nutrition period, the reverse is the case with the breast-fed infants. In spite of this fact, however, the breast-fed children still excrete less nitrogen during the starvation period than the hand-fed children, and the authors draw the conclusion that the former are more capable of resisting the effects of deprivation of food. The excretion of the acetone substances during starvation was also investigated. The amount excreted rapidly increased in the second day of hunger, running nearly parallel with the increased output of nitrogen in the case of the breast-fed children. In the case of the hand-fed children, the acetone substances increased with diminishing nitrogen output. A few measurements of the respiratory exchanges were also made by the authors. S. B. S. `

The Method and Places of Formation of Conjugated Glycuronates in the Organism. JUHO HÄMÄLÄINEN (*Chem. Zentr.*, 1913 ii, 1319—1320; from *Skand. Arch. Physiol.*, 1913, **30**, 196—198).—The small intestine of a rabbit under ether narcosis, after washing, was perfused with Ringer's fluid from the mesenteric artery to the portal vein. *a*-Santenol and dextrose were then injected into the intestine. After six hours' perfusion, the per-

fusion fluid and intestinal contents were examined, and a non-crystalline substance with the properties of α-santanolglucoside was isolated. Glucoside formation appears to take place therefore in the intestinal wall.   S. B. S.

Fat Absorption by the Gastric Mucosa. CHARLES W. GREENE and WILLIAM F. SKAER (*Amer. J. Physiol.*, 1913, **32**, 358—368).— Evidence is adduced that absorption of fats occurs in the stomach of mammals (cats, dogs, rats). The gastric epithelium contains fat even in fasting; this is increased by feeding on fats. The fat in the gland cells, especially in the pyloric region, may be increased by fasting. This has no relation to absorption fat, but is due to mobilisation of the body fat. The observations throughout are histological.   W. D. H.

The Processes of Absorption in the Intestine. N. A. DOBROWOLSKAJA (*Biochem. Zeitsch.*, 1913, **56**, 267—290).—The author discusses the various views as to the method of utilisation of the proteins in the organism, including those of Heidenhain, Hoffmeister, Abderhalden, etc., and attempts by various experimental methods to throw some light on the mechanism. In the first series of experiments, he analyses the serum of portal blood of dogs, estimating the changes of total non-protein nitrogen, and the amino- and peptide-nitrogen produced by the introduction of the chymus obtained from intestinal fistulæ of other animals into the small intestines. No definite results were obtainable by this method, as it was shown that the operative procedure alone, without introduction of digestion products, produced changes in the composition of the serum of the experimental animals. In a second series of experiments, the *in vitro* changes on the amino-nitrogen produced by serum, intestinal extracts, pancreas, etc., on amino-acids and digestion product of proteins, were investigated. The results again lead to no definite conclusions, in some cases indicating synthesis, and in others peptide degradation. In the third series of experiments, an anastomosis was made between the portal vein and the kidneys by the junction of the central end of the *vena lienalis* with the peripheral end of the renal artery. It was assumed that, in the event of introduction of digestion products in the intestine, and a consequent resorption of amino-acids into the portal vein, the excess would be eliminated by the kidneys. To increase the pressure in the kidneys, the portal vein was partly constricted above the junction with the *vena lienalis*. In the majority of cases, the kidney not connected with the portal vein was extirpated. In all of these cases, the animals died. In two cases, when the second kidney was left intact, a certain number of experiments were performed, and the nitrogen of the amino-groups, the hippuric acid, and ammonia nitrogen of the urine excreted were estimated. The introduction of nitrogen into the alimentary tract (by feeding) lead in many cases, especially that of alanine, to an increased amino-nitrogen in the urine. Owing to the fact that the second kidney was intact, these experiments could hardly be considered

satisfactory. In the fourth series of experiments, a portal vein fistula was made according to the method of London and the author, and blood was removed by way of the fistula at various periods after feeding. The results showed a periodic fluctuation in both the portal blood and the blood of the general circulation (removed from the jugular vein). The general result of the experiments is to indicate the difficulty of artificially increasing the amino-nitrogen of the portal vein under conditions approaching the normal physiological. S. B. S.

The Indispensability of Lipoids for Life. The Relation of the Necessary Substances to the Lipoid Extracting Agents. WILHELM STEPP (*Zeitsch. Biol.*, 1913, 62, 405—407 Compare A., 1911, ii, 1002).—This is a continuation of the author's previous work on mice. A mixture of lecithin, cholesterol, kephalin, cerebron, and phytin added to a diet freed from lipoids by alcohol-ether extraction, does not supply the missing necessary material. If the primary acetone extract of egg-yolk is added to lipoid-free food, the result is that the necessary material is still lacking; the same is true for the secondary alcoholic extract. But the primary alcoholic extract restores the value of the lipoid-free food. The materials necessary for life are therefore soluble in alcohol, but not in acetone. If the material is extracted with acetone first, part only of the indispensable material goes into solution; the acetone-soluble substances are soluble also in alcohol. Extraction with ether does not remove the indispensable material; fat is therefore for the mouse not indispensable. Extraction of the food with alcohol entirely removes its power to support life. W. D. H.

Are there Substances at Present Unknown in Food-stuffs which are of Importance for the Maintenance of Life? EMIL ABDERHALDEN and ARNO E. LAMPÉ (*Chem. Zentr.*, 1913, ii, 522—523; from *Zeitsch. gesamte. expt. Med.*, 1913, 1, 296—354).—As a result of a critical experimental investigation on a broad basis of the work of Suzuki, Shimamura and Odake, and of Funk and others, the authors draw the conclusion that up to the present time there has been no absolute proof of the existence of unknown substances in foods, of general significance, which are essential to the maintenance of life. They do not consider that the action of the so-called oryzanin of the Japanese authors, or of Funk's vitamine, has as yet been definitely established. S. B. S.

The Biological Significance of the Fat-content of Fish, with Special Reference to their Habitat. OSW. POLIMANTI (*Biochem. Zeitsch.*, 1913, 56, 439—445).—Attention is called to the fact that during the development of fish embryos, the amount of visible fat diminishes, during which time the habitat gradually alters from that of an organism living on the surface of the water to one living deeper in the sea. It seemed therefore possible that the nectonic fish, which move rapidly about the surface, should contain more fat than the less active, more slowly moving, benthonic fish. Numerous analyses of various species were carried

out, which tend to confirm the above theory, the fat varying from 1·115 to 20·447% of the solid substance. S. B. S.

Proteins of Fish Sperm. ALBRECHT KOSSEL (*Zeitsch. physiol. Chem.*, 1913, **88**, 163—185).—The protamines from the sperm of a number of species of fish have been isolated and investigated. (The figures given are % of total nitrogen.)

Percine from the yellow perch (*Perca flavescens*) contains 85·5% of diamino-acid nitrogen, and 9·8% of monoamino-acid nitrogen, the former being mainly arginine (78·1%) with some histidine (5·6%). No lysine was present. The protamine from the pike perch (*Stisostedion vitreum*) proved to be identical with this.

That from the tunny (*Thynnus thynnus*) (compare Ulpiani, A., 1903, i, 215), which is termed thynnine, contains 80% of arginine nitrogen, no lysine or histidine, and 10% of monoamino-acid nitrogen. The sulphate, like that of other protamines, separates from aqueous solution as an oil. Thynnine also contains tyrosine. *Pelamys sarda* contains a very similar protamine.

The protamine of the sword fish contained 81·5% of arginine nitrogen, and 14% of monoamino-acid nitrogen. Neither histidine nor lysine were present.

The protamine of *Oncorhynchus tschawytscha*, the Chinook salmon (compare A. E. Taylor, A., 1909, i, 344), is identical with the salmine from Rhine salmon (Kossel and Dakin, A., 1904, i, 355, 702).

In the white fish (*Coregonus albus*) the proportions of arginine and monoamino-acid nitrogen are 87·3 and 9·4. In the lake trout (*Salvelinus*) they are 88·9 and 7·1, whilst in *Esocine*, the protamine of the pike (*Esox lucius*), they are 86·3 and 11·3.

In general, these protamines contain two molecules of arginine to one molecule of monoamino-acid—in a few protamines the proportion of monoamino-acids is larger. The protamines are thus to be expressed by the formula a_2m, where a is arginine, or $(alh)_2m$, when all three diamino-acids are present, the proportion of diamino-acid being again as 2 to 1.

A table is given of the known protamines and their formulæ. E. F. A.

The Lipoids of Nervous Tissue. CESARE SERONA and ANOTOINETTE PALOZZI (*Chem. Zentr.*, 1913, ii, 1064—1065; from *Arch. Farm. sperim.*, 1913, **15**, 375—384).—The composition of the brain (white and grey matter) of ox and calf was as follows: 14·25—16·13⁰/₀₀ cholesterol and the esters of cholesterinolic and palmitic acids, 39·8—44·1⁰/₀₀ oleic acid and palmitic acid lecithins, 14·6—14·8⁰/₀₀ cerebrin, and 3·76—5·8⁰/₀₀ homocerebrin or cerasin. To separate the constituents, the following process was employed. The brain was extracted with 5—6 times its weight of a mixture of equal parts of alcohol and ether. From the residue a substance could be extracted with hot alcohol with m. p. 164—165°, which had the properties of homocerebrin or cerasin. The alcohol-ether extract yielded, after evaporation of the ether, a flocculent mass A, and the alcoholic residue on evaporation, a waxy mixture B.

Each of these fractions was treated successively with cold acetone, cold ether, and hot alcohol. The acetone extract was fat-free, and contained, besides some phosphatic lipoids and cerebrin, which became insoluble on solution and reprecipitation with acetone, chiefly cholesterol and its fatty esters. The ethereal extract could be separated into two fractions, one, insoluble in cold alcohol, yielding a substance corresponding with Thudichum's and Koch's kephalin, which appears, on further investigation, to be an impure lecithin mixed with cerebrin, and a soluble fraction, consisting also chiefly of impure lecithin mixed with cerebrin. The alcoholic extract was also separated into fractions soluble and insoluble in cold alcohol. The former consisted of cerebrin, m. p. 190—192°, which on hydrolysis yielded a fatty acid, m. p. 74—75°, presumably cerebrotinic acid, and a reducing sugar with $[a]_D^{20} + 27·5°$, and a substance which is possibly galactosamine. The part soluble in cold alcohol, m. p. 160—165°, is apparently impure homocerebrin or cerasin.　　　　　　　　　　　　　　　　　　　　S. B. S.

Influence of Activity on Automatic Rhythm in Heart Muscle. GEORGE R. MINES (*Proc. physiol. Soc.*, 1913, xiii ; *J. Physiol.*, 47).—If a frog's or mammal's heart is made to beat faster, the subsequent automatic rhythm is slowed; in the octopus the reverse occurs. In both cases, forced activity leads to formation of acid, but in different hearts, and different parts of the same heart, the optimum hydrogen ion concentration is different. In some cases the increase will be towards this value, in others away from it.
　　　　　　　　　　　　　　　　　　　　　　　　　W. D. H.

Hydrogen Ion Concentrations Limiting Automaticity in Different Regions of the Frog's Heart. (Miss) DOROTHY DALE and C. R. A. THACKER (*Proc. physiol. Soc.*, 1913, i—ii ; *J. Physiol.*, 47).—The different heart chambers develop rhythm with varying degrees of hydrogen ion concentration. The sinus will beat in solutions which are too acid for the auricle, and the same holds between auricle and ventricle. Similar differences appear on the alkaline side. The actual figures are given in the paper.　　　W. D. H.

Synthetic Sugar Formation in the Artificially Perfused Liver. GUSTAV EMBDEN, ERNST SCHMITZ and MARIA WITTENBERG (*Zeitsch. physiol. Chem.*, 1913, 88, 210—245).—The perfusion fluid employed was Ringer's solution, containing in it dog's blood-corpuscles washed by centrifugalising. If the liver (dog) is freed from glycogen by phloridzin poisoning, the perfusion leads to a slight but constant formation of sugar. If then dihydroxyacetone is added, the amount of sugar formed (dextrose) is increased. The addition of dl-glyceraldehyde to the perfusing fluid increases the sugar formation greatly; this sugar is in part d-sorbose. The aldehyde appears to be directly transformed into the sugar with previous rupture into short carbon chains. Glycerol forms dextrose less than the two trioses.　　　　　　　　　　　W. D. H.

Formation of Acetoacetic Acid from Acetic Acid [in the Liver]. GUSTAV EMBDEN and ADAM LOEB (*Zeitsch. physiol. Chem.*, 1913, 88, 246—258).—A study of the formation of acetoacetic acid

in the liver indicates that it is not formed from acetic acid by oxidative changes. The presence of *n*-valeric acid or of propionic acid prevents its formation from acetic acid. Formic acid is without influence, and is but little attacked on passing it through the liver. *dl*-Lactic acid has less effect on the reaction than propionic acid.

The conversion of acetic acid into acetoacetic acid is greatly retarded when the liver is full of glycogen. The addition of glycollic acid to the blood stream increases the formation of acetoacetic acid in the liver, although to a less extent than acetic acid.

E. F. A.

The Effect of Pituitary Extract on Renal Activity. C. E. KING and O. O. STOLAND (*Amer. J. Physiol.*, 1913, **32**, 405—416).— The view is disputed that pituitrin directly stimulates the renal epithelium; the vascular changes (vaso-dilatation) are considered sufficient to account for the diuresis.   W. D. H.

The Heat-production of Fatigue and its Relation to the Production of Lactic Acid in Amphibian Muscle. RUDOLPH A. PETERS (*J. Physiol.*, 1913, **47**, 243—271).—By a modification of A. V. Hill's calorimeter it was found that the heat produced by the indirect stimulation of frog's muscles until fatigue set in has a maximum value of about 0·9 cal. per gram of muscle. The heat liberation is roughly exponential, and about 70—80% of it is liberated in the first two minutes. The figure 0·9 is about half of that obtained in chloroform rigor. No processes other than contraction arise in the production of rigor. The lactic acid figures agree with those of Fletcher and Hopkins; heat production and lactic acid liberation are intimately associated.   W. D. H.

The Presence in the Vascular Walls of a Ferment Setting Free a Reducing Sugar at the Expense of the Virtual Sugar of the Blood, and Decomposing Phloridzin. RAPHAEL LEPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, **157**, 627—628. Compare this vol., i, 1274).—The experiments show the presence of a ferment in the vascular walls of the kidneys, lungs, and aorta, capable of setting free a reducing sugar in the blood, a function previously ascribed to the liver alone. The ferment is also capable of partly hydrolysing phloridzin.   W. G.

Amylogenesis and its Relation to Glycolysis in the Animal Organism. CESARE PAUERI (*Chem. Zentr.*, 1913, ii, 1316; from *Arch. Farm. sperim.*, 1913, **16**, 54—96)—From his own results and those of other investigators, the author draws the conclusion that glycogen formation is a necessary preliminary process in the utilisation of sugar in the organism, and that a disturbance of this function results in diabetes mellitus. For the treatment of this condition, therefore, substances must be employed which assist the glycogen formation. Extract of muscles and of pancreas, both alone or combined, were found to be incapable of degrading dextrose at 37°. Disappearance of this substance under these

conditions can be attributed to bacterial action. Lactic and acetic acids were formed from the sugar under the combined action of pancreas extract and micro-organisms. The formation of these acids accounts for the fact that the addition of dextrose inhibits a far-reaching putrefaction of pancreas. No alcohol could be detected as a result of the combined action of pancreas and bacteria on sugar. A fasting animal exhibited appreciable formation of glycogen in the liver. Addition of extract of pancreas did not inhibit sugar formation in the transfusion of a surviving liver.

S. B. S.

A Comparison of the Observed and Computed Heat Production of Cattle. HENRY PRENTISS ARMSBY (*J. Amer. Chem. Soc.*, 1913, **35**, 1794—1800).—Experimental evidence that in the case of men and carnivora the usual equivalence exists between chemical energy, heat energy, and mechanical energy, is already forthcoming, but hitherto such investigations have not, as a rule, included an examination of herbivorous animals.

The present paper gives an account of results obtained during the last decade on cattle (steers), and in the aggregate of fifty-seven experiments the observed heat production differs from the computed by only 0·4%. **D. F. T.**

Constituents of Animals Fats. The Fat of Cervus elaphus. ISIDOR KLIMONT and E. MEISL (*Monatsh.*, 1913, **34**, 1489—1492).— A lard from the red deer, with the following constants, has been examined: D 50°, 0·9066, acid number 20·5, saponification number 203·5, iodine number 19·3, m. p. 48° (Pohl), solidification point 47·5°. The fat was recrystallised eleven times from hot acetone, when β-palmityldistearin, m. p. 62·5—63·5°, was obtained (compare Bömer and Limprich, this vol., i, 442). **J. C. W.**

The Organic Substance in the Skeletal Tissues of Anthozoa. IV. Isolation and Identification of Bromogorgonic Acid. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1913, **88**, 138—154. Compare A., 1907, ii, 283; A., 1908, ii, 310).—3 : 5-Dibromo-*dl*-tyrosine has been identified as a product of the hydrolysis of *Primnoa* gorgonin with barium hydroxide. This is the first organic bromo-compound obtained by the hydrolysis of a naturally occurring protein. The whole of the bromine present in the gorgonin molecule is not dibromotyrosine. Other products of the hydrolysis of gorgonin are tyrosine, glycine, alanine, leucine, aspartic, glutamic, and oxalic acids. **E. F. A.**

The Secretion of Cerebro-spinal Fluid. WALTER E. DIXON and WILLIAM D. HALLIBURTON (*J. Physiol.*, 1913, **47**, 215—242).—An intravenous injection of an extract of the choroid plexuses (choroid gland) produces an increased secretion of cerebro-spinal fluid, as tested by its rate of outflow through a cannula. The active principle is thermostable, soluble in water and in alcohol, and does not pass the pores of a Chamberland filter. Other effects of the

injection are increase of respiration, and a slight fall of blood-pressure. Extracts of brain produce the same effect, but less markedly; no other animal extracts act in the same way. Probably as a result of cerebral activity, some waste product acts as a hormone to stimulate the activity of the choroid cells, and from the richness of the cerebro-spinal fluid in carbon dioxide, it is suggested that one function of the fluid may be to enable the brain to get rid of this material. Reasons are given why this hormone is considered to act on the gland cells and not on secretory nerves. The hormone in question is not found in the cerebro-spinal fluid itself except in cases where catabolism is in excess, as in degenerative processes of the central nervous system.

Other agents which produce an increase of the fluid are excess of carbon dioxide in the blood, and drugs which interfere with respiration. The volatile anæsthetics have a similar action; these may act by interfering with oxygenation or by altering the physical condition of the secreting cells. A large number of substances were investigated, but all the remainder gave negative results, if respiratory and vascular effects were excluded.   W. D. H.

The Comparative Composition of Human and Cow's Milk. EDWARD B. MEIGS and HOWARD L. MARSH (*J. Biol. Chem.*, 1913, **16**, 147—168).—Human milk differs from cow's milk in three important ways. It contains more lactose, less protein, and more substances of unknown nature. The following figures are averages in percentages of the whole milk:

	Fat.	Lactose.	Protein.
Human milk	2 to 4	6 to 7·5	0·7 to 1·5
Cow's milk	2 ,, 4	3·5 ,, 5	2·5 ,, 4

The unknown constituents are soluble in alcohol and ether; they contain little or no nitrogen, and are of importance as food. Some are crystalline, and the crystalline form of one is figured and described at length. (This contains sulphur, but is free from nitrogen.) They are most plentiful in early human milk (1%); as lactation proceeds they sink to 0·5%. Cow's milk at the latter period contains 0·3%. The paper contains analytical tables, and descriptions of methods. Much of the work was done by the late Arthur V. Meigs.   W. D. H.

The Soluble Caseins of Milk. LÉON LINDET (*Bull. Soc. chim.*, 1913, [iv], **13**, 1001—1006   Compare this vol., i, 1116).—Further experiments are quoted in support of the author's views as to the presence of an *a*- and *β*-caseinogen in milk and the relationship between them. The sum of these two substances present is fairly constant in milk, but the proportions of each are very variable.   W. G.

Solubility of the Proteins of Milk in the Elements of the Serum; Reduction of their Solubility under the Influence of Calcium Chloride. LÉON LINDET (*Bull. Soc. chim.*, 1913, [iv]. **13**, 929—935). —The soluble proteins of milk include casein (distinguished as

α-casein), having $[\alpha]_D$ −116°, and a second, called β-casein, which differs only in specific rotation, $[\alpha]_D$ −30°. Milk serum, from which all the proteins had been removed by means of phenol, on evaporation and incineration yielded ash of the following composition, expressed in grams per litre of milk: alkali chlorides, 1·949; alkali citrates (calculated from the carbonate found), 0·765; alkali phosphates, 0·514; calcium phosphate, 0·638; magnesium phosphate, 0·458; iron and aluminium phosphates, 0·108; calcium sulphate, 0·341; undetermined, 0·387. An artificial serum containing lactose, 5; sodium chloride, 0·2; sodium citrate, 0·08; and sodium phosphate, 0·05 per cent., can dissolve 3·456 grams of casein per litre, and probably as much more of the β-casein. In milk, probably all the β-casein is in solution, and about 10% of the α-casein, the rest of the latter being in suspension. The addition of calcium chloride to milk before coagulation by rennet increases the nitrogen and phosphate content of the coagulum and accelerates the action, due to its converting the sodium salts into insoluble calcium salts, and thereby destroying the solvent action of the former on the casein. T. A. H.

Psychic Hyperglycæmia in Rabbits. IVAN BANG (*Zeitsch. physiol. Chem*, 1913. 88, 44—46).—Hirsch and Reinbach (*ibid.*, 1913, 87, 122) have described a hyperglycæmia and glycosuria in rabbits as the result of fright. The non-recognition of this condition produced by psychical causes renders much work on the general subject untrustworthy. The existence of such a psychic condition in rabbits and other animals is confirmed in the present paper.
W. D. H.

Pentosuria from the Chemical Point of View. ERNST ZERNER and RUDOLFINE WALTUCH (*Monatsh.*, 1913, 34, 1639—1652).—In most cases of pentosuria which have been investigated, optically inactive urines have been encountered, from which osazones apparently corresponding with *i*-arabinose or *l*-arabinose have occasionally been isolated.

Two new cases of pentosuria have now been examined. The urines were inactive, which is taken as an indication of the absence of *l*-arabinose, since this has a very high specific rotation. The osazone obtained had m. p. 162—163°, and a small *d*-rotation, which was insufficient to distinguish it from *d*-arabinosazone. Diphenylmethanedimethyldihydrazine (Braun, 1910, i, 525) gave no indication of arabinose. A mixture with an equal weight of *l*-xylosazone had m. p. 208—210°, whereas *i*-xylosazone has m. p. 210—215° (Fischer, A., 1894, i, 566). The osazone from these urines is therefore *d*-xylosazone, and very probably the pentose is *d*-xylose. Further experiments are being carried out definitely to determine the nature of the sugar. J. C. W.

The Sugar in Pentosuric Urine. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, 56, 506—507).—Zerner and Waltuch (preceding abstract) have maintained that the sugar isolated by them in a

case of pentosuria was *d*-xylose, as the mixture of its osazone with that of the corresponding *l*-derivative has a higher melting point than the pure substance. A mixture of the *l*-form of osazone with the osazone obtained from the urine of the cases of pentosuria of the author did not produce a corresponding rise in the melting point. The author does not see, therefore, any reason to suppose that the sugar in his case is other than the *dl*-arabinose, as originally suggested. It is conceivable that various forms of pentosuria exist.   S. B. S.

Physiological Action of Colloidal Carbon. GUIDO IZAR and C. PATANÉ (*Biochem. Zeitsch.*, 1913, **56**, 307—318).—The so-called mellogen, produced by the disintegration of a carbon anode by a galvanic current, was used in these experiments. It can be dispersed in water made slightly alkaline by sodium hydroxide, which mixture is afterwards neutralised by passing in carbon dioxide and heating. This preparation has no influence on the total autolysis of the liver. It increases the amount of uric acid formed by autolysing ox-spleen and liver, and inhibits the uricolytic action of ox-kidneys and washed pulp of dog's liver. Intravenous injections of large quantities into rabbits, white rats, pigeons, etc., produce dyspnœa, but only a few of the animals succumb. The intravenous injection has no appreciable effect on body temperature (rabbits), but increases the amount of carbon dioxide in expired air (as compared with control injection of distilled water). The amount of increase is approximately proportional to the amount of mellogen injected.   S. B. S.

Action of Colloidal Sulphur on Autolysis. ANTONIO FAGIUOLI (*Biochem. Zeitsch.*, 1913, **56**, 291—294).—Colloidal sulphur increases the autolysis of liver tissue (ox, dog, and monkey), and to a still larger extent that of tumour tissue (rat sarcoma and human liver carcinoma).   S. B. S.

Pharmacological Action of Ethyl Alcohol on the Isolated Mammalian Heart at Different Temperatures. GIUSEPPE BRANDINI (*Chem. Zentr.*, 1913, ii, 524; from *Arch. Farm. sperim.*, 1913, **15**, 178—192, 193—212).—The experiments were carried out on a rabbit's heart in a Langendorff perfusion apparatus. At normal temperatures the alcohol in small doses (1 in 50,000—1,150,000) exerts a stimulant action, in medium doses, the heart activity is depressed, but in higher concentrations ($30^0/_{00}$) the action is toxic. At lower temperatures (33°) the effect is weaker, and higher concentrations of alcohol are required to produce the same effects described as resulting at 37°.   S. B. S.

The Scission of the Benzene Ring in the Animal Body. II. Behaviour of Muconic Acid and Benzene in Liver-perfusion Researches. MARIE HENSEL and OTTO RIESSER (*Zeitsch. physiol. Chem.*, 1913, **88**, 38—43).—When muconic acid is added to a fluid employed for perfusing the liver, the amount of acetone formed

by that organ is greatly increased, it may be fourfold. No certain result was obtained by perfusing the liver with benzene; this substance is strongly toxic. W. D. H.

The Conjugated Excretion Products of Bromobenzene and *p*-Iodophenol. ERBERTO ANGELO RABBENO (*Chem. Zentr.*, 1913, ii, 1070; from *Arch. Farm. sperim.*, 1913, **15**, 535—546).—It was presumed that it should be possible, by the estimation of the total sulphur, the conjugated sulphuric acid, and the rotation of the urine of dogs, to which bromobenzene and *p*-iodophenol had been administered *per os*, to ascertain whether the halogen derivatives of benzene undergo conjugation with glycuronic acid as well as with cystine and sulphuric acid. It was found as a result of the experiments that the bromine derivative is excreted conjugated only with cysteine and sulphuric acid, whereas the iodo-derivative is excreted conjugated with glycuronic and sulphuric acids, but not with cysteine. S. B. S.

The Influence of the Administration of Creatine and Creatinine on the Creatine Content of Muscle. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1913, **16**, 169—186).— The subcutaneous administration of creatine to rabbits causes a small increase in the creatine content of muscle (about 5% in five experiments). This is quite insufficient to account for the creatine, which does not reappear in the urine. The administration of creatinine exerts a similar effect, the creatine content of the muscles being 6% above the normal, an amount sufficient to account for the creatinine which was not eliminated by the kidneys. This apparent increase in the muscular creatine was not due to a retention of unchanged creatinine. Of the creatine given, 25—80% (the quantity depending on the amount injected) reappeared in the urine unchanged, whilst 2—10% was eliminated as creatinine. When creatinine was administered, 77—82% (average 80%) reappeared in the urine, and no elimination of creatine was detected. W. D. H.

Narcosis and Oxygen Consumption. JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1913, **56**, 295—306).— The authors discuss the relationship between inhibition of oxidation and narcosis. When the embryos of *Fundulus* are not narcotised, they respond by rapid movement to a stimulus of $N/25$-hydrochloric acid. It was found that they only become insensitive to this stimulus when their oxidation rate has been reduced to 1/14 of the normal value by potassium cyanide; a reduction by this method to 1/9 is without influence on their response to the stimulus. On the other hand, they become unresponsive to chloroform treatment, without any appreciable reduction of the oxidation rate. Ethyl ether and butyl alcohol can produce insensitiveness to the strongest stimuli with the diminution of the oxidation rate by only 26%. Medusæ loose their mobility and reactivity to stimuli by direct reduction of oxidation by potassium cyanide only

when this reduction is 3—6 times as great as that which results when the motility and reactivity are destroyed by ethylurethane. The conclusion is drawn that narcosis cannot be due directly to reduction of oxidative capacity, and that the latter is a result either of inactivity of the tissues due to narcosis, or it is a secondary action of the narcotis, which stands in no direct relationship to the narcosis itself.   S. B. S.

Biological Oxidation of Certain Glucosides. Juho Hämäläinen (*Chem. Zentr.*, 1913, ii, 1319; from *Skand. Arch. Physiol.*, 1913, **30**, 187—190).—After injection of the glucosides of certain terpene alcohols, the corresponding glycuronates appear in the urine. There is therefore no preliminary scission of the glucoside into sugar and alcohol, for neither in the blood nor in the organs could any terpene be detected. On the contrary, both glycuronate and the corresponding glucoside could be found. The facts confirm the theories of Fischer and Piloty and of Sundvik on the formation of conjugated glycuronates in the organism. Furthermore, more glycuronate is excreted after administration of the glucoside than after administration of the free substance.   S. B. S.

The Influence of Certain Quinoline and Naphthaquinoline Derivatives on the Excretion of Uric Acid. Riccardo Luzzato and Riccardo Ciusa (*Chem. Zentr.*, 1913, ii, 1318—1319; from *Arch. Farm. sperim.*, 1913, **16**, 6—40).—The following derivatives were investigated : 2-*p*-methoxyphenylquinoline-4-carboxylic acid, 2-*p*-dimethylaminophenylquinoline-4-carboxylic acid, 6-amino-2-phenylquinoline-4-carboxylic acid, 3-phenyl-β-naphthaquinoline-1-carboxylic acid, 2-*p*-dimethylamino-β-naphthacinchonic acid, 2-phenyldihydro-β-naphthaquinoline-4-carboxylic acid, 2-*o*-hydroxylphenyl-β-naphthacinchonic acid, 3-phenyl-β-naphthaquinoline, and 2-phenylcinchonic acid (atophan). Of these it was found that 3-phenyl-β-naphthaquinoline-1-carboxylic acid (the so-called diapurin) and atophan caused an intense excretion of uric acid, the action of the latter being somewhat less than that of the former. It caused, however, no turbidity of the urine, and was better tolerated, and a dose of 5 grams caused no bad symptoms in a dog of 12 kilos. weight, and could be taken by a man in doses of 2 grams for several days without ill effects. The action of diapurin is attributed to the mobilising effects on the uric acid, which already exist in the organism as a result of purine degradation, as the increased excretion of the acid is not accompanied by an increased phosphoric output, which should result if the nucleins are broken down. Furthermore, the increased output of uric acid ceases two or three days after administration of the drug. The particular action on the uric acid is due to the presence of a phenyl group in the 2-position, the quinolinecarboxylic acid group being inactive. The action is neutralised by the presence of the methoxyl and amino-groups in the 6-position. On the other hand, 2-phenyl-6-methylquinoline-4-carboxylic acid (paratophan) and 8-methoxy-2-phenylquinoline-4-carboxylic acid (isatophan) are fairly active. The introduction of the OH,

NMe$_2$, or OMe group into the 2-phenyl ring inhibits or weakens the action on uric acid. As hydroxyphenylquinoline-4-carboxylic acid is, according to Sk'orczewski and Sohn, a degradation product of atophan, the latter appears to exert its influence before oxidation. The reduction of the pyridine ring destroys or weakens the action. The general methods of Doebner, Kuntze, Lachs, and Steinert were employed in the preparation of the compounds, and the following substances were obtained: 2-p-*anisylquinoline-4-carboxylic acid*, m. p. 217°; 2-*dimethylaminophenylquinoline-4-carboxylic acid*; 6-*amino-2-phenylquinoline-4-carboxylic acid*, m. p. 160° (decomp.).

S. B. S.

The Behaviour of Certain Rhamnosides in the Animal Body. MARIO GARINO (*Zeitsch. physiol. Chem.*, 1913, **88**, 1—8).—Rutin, quercitrin, hesperidin, and hesperetin, after intravenous or oral administration, pass through the animal organism, and are excreted almost entirely unchanged. Hydrolysis of these substances appears to occur either not at all, or in the merest traces, in the body.

W. D. H.

The Action of Strophanthin on the Excised Frog's Heart. A. J. CLARK and GEORGE R. MINES (*Proc. physiol. Soc.*, 1913, vii—viii; *J. Physiol.*, 47).—The effect of perfusing the heart with one part of strophantin in a million of Ringer's fluid is at first beneficial, and later toxic. The observations were made on the mechanical activity of the ventricle, the length of the A.V. interval, and on the electrical concomitant of activity.

W. D. H.

Mechanism of the Biological Action of the Röntgen Rays. EUGEN PETRY (*Biochem. Zeitsch.*, 1913, **56**, 341—352).—The author has investigated the influence of Röntgen rays on the toxicity of various metals, following a similar line of research to that of Tappeiner and his pupils on the sensitising influence of eosin on actinic rays. Amœbæ obtained from hay-infusion were used as the objects of experiments, and these were submitted to the action of uranium nitrate, sodium tungstate, zinc sulphate, and colloidal zinc sulphide in the dark, in the presence and the absence of Röntgen radiation. As a result, it was found that the rays had no appreciable effect in increasing the toxicity of the metals. Compounds were purposely chosen which fluoresce when submitted to radiation. The rays exerted no action on the sensitising activity. Experiments were also carried out to ascertain whether organs which are highly sensitive to Röntgen rays contain substances which act as light-catalysts for these rays. Testicles and lymph glands were chosen, and the effect of radiated and unradiated extracts on hæmolysis, the mobility of amœbæ, and the milk-clotting by rennin, were investigated. The results were negative, and the author draws the conclusion that no substances have been discovered which act as catalysts for the Röntgen rays in the same way that eosin acts as catalyst for actinic rays. S. B. S.

Purine and Xanthine Bases as Intermediary Products in Poisoning by Nucleoproteins. HENRI DE WAELE (*Chem. Zentr.,* 1913, ii, 519—520 ; from *Zeitsch. Immun. expt. Therapie,* 1913, **18,** i, 410—422).—Just as, according to the author, the proteins use the amino-acids as intermediary products in developing their thromboplastic action, the nucleoproteins act by intermediation of the purine bases. Thus nucleoproteins, otherwise harmless, can be rendered toxic by degradation of their molecule, or by the addition to them of degradation products, or even amino-acids. Under these conditions, curves were obtained similar to those described by the author for proteins, showing, in an oscillatory manner, thromboplastic and antithrombic phases. The first of these is short, and may be overlooked. The nucleins produce a strong antithrombic secretion. The antithrombic phase is of short duration, but produces a distinct, although short-lasting, immunity. The nucleoproteins can be activated either by purines (affecting the nucleic acid part of their molecule) or by amino-acids (affecting the protein part). Nucleohistones, owing to the presence of the histone group, are directly toxic. For many nucleoproteins, such as those from the thymus, animals are directly anaphylactic, in the same way that carnivora are sensitive to peptones.   S. B. S.

The Removal of the Poisonous Properties of Protein Cleavage Products by Substitution of the Cyclic Nucleus. GEORGE BAEHR and ERNST P. PICK (*Arch. expt. Path. Pharm.,* 1913, **74,** 73—91).—The proteins of horse- and ox-serum yield, on gastric digestion, poisonous products. But if these proteins are iodised, nitrited, or diazotised, the products of pepsin digestion no longer produce "peptone-shock," causing neither fall of arterial pressure nor loss of coagulability in the blood. The iodine, nitro- and diazogroups in question enter the cyclic nucleus of the protein molecule.
                                                                W. D. H.

Nature of the Coagulant of the Venom of Echis carinatus, a Small Indian Viper. J. O. WAKELIN BARRATT (*Proc. Roy. Soc.* 1913, [*B*], **87,** 177—190).—The effect of the intravenous injection of thrombokinase is essentially different from that of injection of thrombin. The latter causes an abundant intravascular formation of fibrin and a reduction of the amount of fibrinogen in the circulating fluid. Little or no fibrinogen is removed after the injection of thrombokinase, which thus has an essentially different action on blood plasma than on a solution of fibrinogen *in vitro* in presence of calcium chloride, which it causes to coagulate. The coagulant of viper venom, as exhibited by its effect in causing intravascular separation of fibrin when injected into the bloodstream and also indicated by its behaviour when heated, is a thrombin and not a thrombokinase.   E. F. A.

Chemistry of Vegetable Physiology and Agriculture.

Biochemistry of Micro-organisms. VIII. Fermentation of Formic Acid by Bacillus Plymouthensis in a Medium of Constant Composition. HARTWIG FRANZEN and FRITZ EGGER (*Zeitsch. physiol. Chem.*, 1913, **88**, 73—102. Compare this vol., i, 322; A., 1912, ii, 669).—Further data are given obtained from experiments with *B. Plymouthensis*, made in the same way as previously with *B. kiliense* and *B. prodigiosus*. The results show the same divergence in different series of cultures. *B. Plymouthensis* ferments formic acid during the first twenty-four hours. The maximum amount of formic acid fermented was 9·95% at 17°, 16·8 and 26·47% at 21°, and 22% at 27°. No general conclusions are drawn.   E. F. A.

Chemistry of Bacteria. II. SAKAE TAMURA (*Zeitsch. physiol. Chem.*, 1913, **88**, 190—198).—*Mycobacterium laticola* contains the same organic constituents whether it is grown on nutritive bouillon or on a medium lacking protein. The aromatic units in its composition are formed in quantity when only short open-chain carbon compounds are supplied as food—for example, lactic acid, glycerol, asparagine.

The inorganic constituents of the cells of *Bacterium tuberculosis* or of *Mycobacterium laticola* undergo considerable quantitative variation according to the nature of the environment in which the culture is made.   E. F. A.

Violet Colouring Matter and its Production by a Certain Bacterium. W. J. HARTLEY (*Sci. Pr.·c. Roy. Dubl. Soc.*, 1913, **14**, 63—73).—The pigment of a bright, violet bacterium obtained from a creamery water has been examined. The pigment turns green with acid, blue with alkali; it does not dye silk. The absorption spectrum has been characterised; it has no bands in the ultraviolet, absorbs continuously the rays in the red less refrangible than λ 6600, and transmits nearly all the rays from λ 6600 to λ 6439. The cultures, when macerated, gave a positive test with picrate paper for hydrogen cyanide.   E. F. A.

Influence of Radioactivity on Nitrogen-fixing Micro-organisms or on those Transforming Nitrogenous Substances. JULIUS STOKLASA (*Compt. rend.*, 1913, **157**, 879—882).—Air activated by pitchblende has a markedly favourable influence on the fixation of atmospheric nitrogen by *Azotobacter chroococcum*, the influence being slightly more favourable with weak radioactive intensity than with a stronger intensity. On the other hand, the transformation of organic nitrogen into ammoniacal nitrogen and the fixation of free nitrogen is much weaker in solutions submitted to the influence of β- and γ-rays than in control solutions.

Soil submitted to air charged with radium emanations showed an increased nitrogen content of 0·021% over the control sample. The reduction of nitrates by denitrifying bacteria is considerably lessened under the influence of radium emanation, although there is ample development of the denitrifying bacteria.   W. G.

Butylene-glycol Fermentation of Dextrose by Staphylococci and Tetragenes. M. LEMOIGNE (*Compt. rend.*, 1913, **157**, 653—655. Compare A., 1912, ii, 1199).—Staphylococci and tetragenes only attack carbohydrates slowly, and do not develop unless they have an abundant supply of organic nitrogenous food. The products of the fermentation of the sugar are dimethyl diketone, acetylmethylcarbinol, and butylene $\beta\gamma$-glycol.   W. G.

The Optical Behaviour of Yeast Maceration Juice. CARL NEUBERG and P. ROSENTHAL (*Biochem. Zeitsch.*, 1913, **56**, 498—500).—The maceration juices from Lebedev's preparations were found to vary when freshly prepared from $-0\cdot10°$ to $-0\cdot42°$ in optical rotation. On keeping, the optical rotation of the juices diminished in some cases, whereas in others it increased. S. B. S.

Osmotic Pressure and Electrical Conductivity of Yeast, Beer, and Wort HENRY H. DIXON and WILLIAM R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **14**, 9—12).—Pressed yeast gives higher values than wort, both in osmotic pressure and electrical conductivity. Comparing beer and wort, it is shown that whilst the electrical conductivity remains the same, the osmotic pressure becomes three times as great during fermentation.   E. F. A.

Extraction of Zymase by means of Liquid Air. HENRY H. DIXON and WILLIAM R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **14**, 1—8).—Immersion of yeast in liquid air from ten to fifteen minutes renders the protoplasm permeable. On thawing, the yeast liquefies, and after centrifuging, the sap of the cells is obtained as a faintly opalescent, brown liquid. This contains zymase in as active a form as that prepared by Lebedev's maceration method. The amount of zymase extracted may be increased by dilution and maceration. The sap is practically free from glycogen, and does not show autofermentation.

The sediment froths actively, due to hydrolysis of the glycogen in the cells and fermentation of the sugar formed.   E. F. A.

The Complete Hydrolysis of Yeast Albumin. HANS PRINGSHEIM (*Woch. Brauerei*, 1913, **30**, 399—400).—The hydrolysis of yeast furnished the following compounds, which were obtained by distillation in the form of esters (Fischer's method). The esters obtained from leucine and valine were the chief product; those from proline, phenylalanine, and glutamic acid were obtained in small quantities; the presence of serine is considered questionable, whilst alanine and glycine were not apparently present.

F. M. G. M.

Influence of Acids on Alcoholic Fermentation. M. ROSENBLATT and (Mme.) M. ROSENBLATT (*Bull. Soc. chim.*, 1913, [iv], 13, 924—929. Compare A., 1909, ii, 752; 1910, ii, 643; Johannesohn, this vol., i, 143).—None of the acids tried has any accelerating action on the activity of yeast, and each of them begins to retard the activity at the concentrations quoted: Hydrochloric ($M/6000$), formic ($M/5000$), acetic ($M/300$), propionic ($M/250$), n-butyric ($M/200$); sulphuric ($M/6000$), tartaric ($M/1000$); phosphoric ($M/5000$), citric ($M/3000$). Potassium hydrogen sulphate behaves similarly. The following salts accelerate the activity, and the optimal concentrations are quoted: Potassium hydrogen oxalate ($M/200$), dipotassium hydrogen citrate ($M/10$), potassium dihydrogen citrate ($M/5$), sodium dihydrogen tartrate ($M/4$), potassium dihydrogen phosphate ($M/3$). T. A. H.

Formation of Acid by Fermentation. ED. MOUFANG (*Zeitsch. f. ges. Brauwesen*, 1913, 36, 297—299).—Dilute solutions of dextrose, lævulose, maltose, and sucrose were treated with yeast in the presence of malt, and the acids formed subsequently estimated by methods which have been described by Mösslinger. F. M. G. M.

Reduction of Chloral Hydrate by Yeast During Alcoholic Fermentation. CARL J. LINTNER and H. LÜERS (*Zeitsch. physiol. Chem.*, 1913, 88, 122—123).—Living yeast in the act of fermenting sucrose reduces added chloral hydrate to trichloroethyl alcohol. E. F. A.

The Uselessness of Zinc for the Culture of Aspergillus niger. CHARLES LEPIERRE (*Compt. rend.*, 1913, 157, 876—879).— *Aspergillus niger* will grow on a culture medium, free from all traces of zinc, providing the ratio, volume of liquid/surface exposed, is always greater than 2. If this ratio falls below 2, however, then the maximum growth is never obtained. This explains the difference between the author's results and those of Javillier (compare A., 1908, ii, 317), who grew the mould on liquid where the ratio v/s was 1·5. W. G.

Polyatomic Alcohols as Sources of Carbon for Lower Fungi. RAY E. NEIDIG (*J. Biol. Chem.*, 1913, 16, 143—145).—Methyl alcohol and ethylene glycol are not capable of producing normal cultures of *Aspergillus* and other moulds when they are introduced into Czapek's medium in place of sugar. Glycerol is readily available, and gives cultures as good as when sucrose is employed. With increasing carbon, the availability does not increase; adonitol, for example, does not compare favourably with glycerol or even erythritol, and two of the hexatomic alcohols failed to yield cultures equal to those on glycerol. No connexion between availability and carbon asymmetry could be established. There may, however, be some relation between availability and the nature of the intermediate oxidation products, since all the substances which are available, including glycerol, yield oxidation products containing one or more asymmetric carbon atoms. W. D. H.

Attempts to Produce Citric Acid from Alcohol and Lactose by Fungi. CARL WEHMER (*Chem. Zeit.*, 1913, **37**, 1393—1394. Compare Mazé and Perrier, A., 1904, ii, 676; Herzog and Polotzky, A., 1909, i, 285; Wehmer, this vol., i, 229).—Unsuccessful attempts are recorded to produce citric acid from alcohol or from lactose by means of fungi. The author thus confirms Herzog and Polotzky's conclusion with regard to the non-formation of citric acid from alcohol (contrast Mazé and Perrier), but differs from them in finding that it is also not produced from lactose.

Two species of *Citromyces* were grown during several months in a nutrient solution containing ammonium nitrate, potassium phosphate, magnesium sulphate, calcium carbonate, and alcohol (2·5 and 5%). The latter exerts a marked retarding effect on the growth of the fungi, which differs in extent for the two species. Citric acid could not be detected.

Under similar conditions, a like result was obtained with lactose solutions, in which, however, growth of the fungi occurred readily.

H. W.

Disinfectants which Dissolve Lipoids. JOSEF GÖSSL (*Zeitsch. physiol. Chem.*, 1913, **88**, 103—108).—Overton and Meyer pointed out that certain anæsthetics owe their activity to the fact that they are soluble in the cell-lipoids. A large number of chemical substances are examined in the present research to see if this also holds for their disinfecting powers, with the result that the answer is in the affirmative. The experiments were made on yeast cells.

W. D. H.

Nitrate and Nitrite Assimilation. OSKAR BAUDISCH (*Zeitsch. angew. Chem.*, 1913, **26**, 612—613. Compare A., 1911, ii, 523; 1912, ii, 286; this vol., i, 324).—Some new experiments in support of the view that nitroxyl, NOH, plays an important part in the assimilation of nitrogen have been carried out, partly on the heights of Monte Rosa, where the activity of the light was nearly equal to that of a mercury lamp. It was found that the liberation of oxygen from solutions of potassium nitrite or nitrate was greatly accelerated by carbon dioxide. Nitric oxide in presence of formaldehyde or methyl alcohol soon produced formhydroxamic acid. Nitric oxide and water, with yellow phosphorus as catalyst, gave ammonium nitrate in sunlight, and ammonium nitrite in mercury light. Nitric oxide itself was detected in moist air which had been passed through dilute alkali and then exposed to brilliant sunlight. Substances of the nature of α-amino-acids were obtained by the action of mercury light on potassium nitrite in presence of carbon dioxide, with ferric chloride as catalyst. A new course for the photo-synthesis of organic substances from air, carbon dioxide, and water is thus indicated. Ammonia was oxidised to nitrous acid in presence of oxygen under the influence of mercury light.

A diagram is given which summarises the numerous photo-reactions between simple carbon, nitrogen, and oxygen compounds, which Baudisch, Piloty, and Stoklasa have already discovered.

J. C. W.

The Influence of Sodium Sulphate on the Growth of Plants. EMIL HASELHOFF (*Landw. Jahrb.*, 1913, **44**, 641—650).— An account of numerous culture experiments undertaken for the purpose of demonstrating the influence of sodium sulphate on the growth of *Vicia faba*, *Phaseolus vulgaris*, *Hordeum vulgare*, and *Zea mays*; the results are exhibited in tabular form.

F. M. G. M.

Uniformity of Structure of the Proteins. Their Changes in Vegetable and Animal Organisms. DMITRI N. PRIANISCHNIKOV (*Bied. Zentr.*, 1913, **42**, 679—682; from *J. exper. Landw.*, 1912).— Certain plants, such as barley, when supplied with ammonium chloride produce amides at the expense of proteins, whilst the ammonia is also converted into asparagine or glutamine. No accumulation of ammonium salt takes place. In the case of peas and vetches, ammonium salts do not increase the amount of asparagine, and may even diminish it. When, however, calcium carbonate is supplied along with an ammonium salt, the latter is converted into asparagine. With lupines, the presence of ammonium salts, both alone and with calcium carbonate, diminishes the amount of asparagine, whilst the plant accumulates ammonia, chiefly from cleavage products of the proteins.

Lower plants can accumulate ammonia without injurious effects. In lower animals proteins are degraded to ammonium salts, which are not completely converted into amides. N. H. J. M.

Effect of Chloroform on the Respiratory Exchanges of Leaves. D. THODAY (*Ann. Bot.*, 1913, **27**, 697—717).—Different varieties of leaves, when treated with small amounts of chloroform, showed increased absorption of oxygen and a similarly increased production of carbon dioxide. In starved leaves the stimulation was generally prolonged.

When the amount of chloroform was sufficient to cause visible disorganisation, the production of carbon dioxide was diminished, whilst the absorption of oxygen was no longer closely correlated with the production of carbon dioxide.

Leaves of *Tropaeolum*, which contain no tannin, showed a depression of oxygen absorption greater than that of the production of carbon dioxide. In leaves of cherry, Portugal laurel, and *Helianthus*, which contain tannins, the absorption of oxygen was very rapid for a short time, and, although quickly falling, remained at a much higher level than the production of carbon dioxide.

N. H. J. M.

Methyl Alcohol of Leaves. MAURICE NICLOUX (*Bull. Soc. chim.*, 1913, [iv], **13**, 939—943).—The author has applied his method (this vol., ii, 1080) to distillates from various leaves, and has found the following quantities of methyl alcohol: ivy, 0·36 gram; spindle-tree (*Euonymus*), 0·45 gram, per kilo. of leaves. In the case of the ivy leaves, the calculations give a negative quantity for formaldehyde, due possibly to the presence of a small quantity of

ethyl alcohol or some similar substance which consumes potassium dichromate without yielding carbon dioxide. It is suggested that methyl alcohol may originate in plants in accordance with the equation $CO_2 + 2H_2O = CH_3 \cdot OH + O_3$. Such an action would require a chlorophyll coefficient above 1, and thus be in harmony with Maquenne and Demoussy's observations (this vol., i, 232 and 429).   T. A. H.

Oxydases and their Inhibitors in Plant Tissues. WILLIAM R. G. ATKINS (Sci. Proc. Roy. Dubl. Soc.. 1913, 14, 143—156. Compare Keeble and Armstrong, A., 1912, ii, 673; this vol., i, 325, 803).— The absence of a brown colour in the sap expressed from plant tissues may be due: (1) to the absence of organic peroxide; (2) to the presence of tannin, preventing the action of the oxydase; or (3) to the presence of some reducing agent or inhibitor. It is considered that oxydase is concerned in the production of cork and sclerenchyma. The distribution of oxydase and of a reducing agent in Iris species is described. The colours of Iris are due to the presence or absence of a yellow plastid pigment and an anthocyan pigment. A reducing substance active in aqueous solution may inhibit the production of anthocyan pigment.
E. F. A.

The Presence of a New Diastase, Salicinase, in Almonds. GABRIEL BERTRAND and ARTHUR COMPTON (Compt. rend., 1913, 157, 797—799. Compare A., 1912, i, 592).—From a study of the temperature and the reaction of the medium, which, under definite conditions, favour the greatest activity of preparations of emulsin from almonds on salicin, the authors consider that their results point conclusively to the presence of a specific enzyme, salicinase, capable of hydrolysing salicin.   W. G.

Flower Pigments of Antirrhinum majus. II. Pale Yellow or Ivory Pigment. MURIEL WHELDALE and HAROLD LLEWELLYN BASSETT (Biochem. J., 1913, 7, 441—444).—The pale yellow or ivory pigment present in each of the main classes of varieties of Antirrhinum with the exception of the white is identified as apigenin. In the plant it exists as a glucoside, and is present in the inner tissues.   E. F. A.

The Trypsin of Calotropis procera R.Br. and the Poison which Accompanies It. C. GERBER and P. FLOURENS (Compt. rend., 1913, 157, 600—603).—The latex of Calotropis procera contains a proteolytic enzyme, which is very resistant to heat, and more active in alkaline than in neutral medium. It coagulates milk, and digests casein and fibrin. Separated from the latex by the usual methods, it is eight to ten times less active than the latex itself, owing to its lability towards the agents used in the separation. Its physiological action varies according to the animal used, and is due to a poison which accompanies it. Subcutaneously injected into a white rat, a rabbit or a fowl, it produces only a local effect

on the skin and muscle, which disappears in a few days. In the case of the guinea-pig, pigeon, and certain cold-blooded animals, it is rapidly fatal. The deaths and premonitory symptoms are similar in character to those observed with the latex of *Broussonetia papyrifera*. The toxic substance can be extracted in the form of a brown solid, by maceration with alcohol.   W. G.

Partial Decomposition of Yeast-nucleic Acid by the Press Juice of Cortinellus edodes. KWANJI TSUJI (*Zeitsch. physiol. Chem.*, 1913, **87**, 379—381).—The pressed juice of the fungus *Cortinellus edodes* produces guanosine from yeast-nucleic acid, indicating that it contains enzymes converting nucleic acid into nucleosides and hydrolysing the latter.   E. F. A.

Capoc and Acon and their Bitter Constituents, Waxes, and Resins. HERMANN MATTHES and LOTHAR STREICHER (*Arch. Pharm.*, 1913, **251**, 438—452).—An examination of capoc and acon fibres. Java capoc, in contrast to cotton, contains cellulose 64·3%, lignin 13%, and pentosans 23—24%. Capoc and acon fibres are brittle, and contain 8·6% and 7·2% respectively of moisture, and about 5—10% of constituents soluble in water. Acon wax (4·63%), m. p. 30·5°, n_D^{40} 1·4682, acid number 65·09, ester number 106·43, saponification number 171·52, iodine number 70·52, Reichert-Meissl value 1·76, Polenske value 1·05, contains about 31% of unsaponifiable constituents, consisting of melicyl alcohol, a *hydrocarbon*, $C_{20}H_{42}$, m. p. 69° (probably laurane), and liquid and solid phytosterols; from the latter, a *phytosterol*, m. p. 136°, and another, m. p. 170° (probably stigmasterol), have been isolated. The fatty acids obtained from acon wax consist of about 20% of solid, and about 80% of liquid, acids. The solid acid consists only of palmitic acid; the liquid acids contain about 61% of oleic acid, 38% of linolic acid, and 1% of linolenic acid.

Capoc wax, m. p. 24°, n_D^{40} 1·4618, acid number 59·85, ester number 110·29, saponification number 170·14, iodine number 69·44, Reichert-Meissl value 2·02, Polenske value 0·97, contains about 28% of unsaponifiable constituents, and yields about 15% of palmitic acid, and 85% of liquid acids similar to those obtained from acon wax.

Capoc and acon possess a bitter taste. This is due to a substance which has been isolated from acon. It is a yellow substance, which is strongly poisonous, dissolves in water, reduces ammoniacal silver oxide and Fehling's solutions, develops with sulphuric acid and potassium dichromate a blue colour changing to green, and gives precipitates with the alkaloidal reagents, although it does not contain nitrogen. It resembles picrotoxin in being decomposed by boiling chloroform into a soluble and an insoluble component. Acon fibres contain chlorophyll and a resin.   C. S.

The Existence of a Cyanogenetic Compound in a Member of the Papaveraceæ (Papaver nudicaule). MARCEL MIRANDE (*Compt. rend.*, 1913, **157**, 727—729).—The author has examined the

leaves of plants of *Papaver alpinum*, of hybrids between this and *P. nudicaule*, and of nearly pure *P. nudicaule* for a cyanogenetic compound. The aqueous distillate of the leaves contains hydrocyanic acid in the case of the hybrids and *P. nudicaule*, but none in the case of *P. alpinum*. The plants with yellow flowers contain more of this compound than those with red or white flowers, and the nearer the plant is to the pure type, *P. nudicaule*, the higher is the yield of hydrogen cyanide. This is the first instance of a member of the Papaveraceæ containing a cyanogenetic compound.   W. G.

Robin and the "Phasin" of Robinia Seeds. ROBERT KOBERT *Landw. Versuchs.-Stat.*, 1913, **79-80**, 176—181. Compare succeeding abstract.—The name "robin" was applied by Kobert to a protein first prepared from the bark of *Robinia pseudacacia* by Power in 1889 (*Pharm. Rundschau*, 1890, **8**, 29), and subsequently characterised more completely by the same author (A., 1901, ii, 679), who showed especially (1) that it was toxic, but lost its poisonous properties when heated; (2) that it hydrolysed amygdalin and sinigrin; and (3) coagulated milk like rennet ferment. These observations, especially as regards the physiological action of the substance, were confirmed and extended by Lau (*Diss.*, Rostock, 1906 (?1901)), Ehrlich (*Klin. Jahrb.*, 1898, **6**, 315), and others, including the present author. In the present paper it is shown: (1) that "robin" undoubtedly behaves as a agglutinant with blood of various kinds; (2) is not toxic when injected subcutaneously into rabbits in quantities of 1 to 10 c.c. of a 4% solution; (3) does not hydrolyse sinigrin; (4) does not coagulate milk; and (5) does not precipitate ricin-serum. The toxicity of the "robin" preparations examined by Lau is ascribed to impurity or to the use of abnormally large doses of the material. The toxicity of the bark, it is suggested, may be due to the alkaloid or the glucoside it contains. From Robinia seeds a similar "phasin," which agglutinates blood, but is not toxic and has no glucosidolytic activity, has been prepared.   T. A. H.

Poisonous Constituent of the Bark of Robinia pseudacacia. FREDERICK B. POWER (*Amer. J. Pharm.*, 1913, **85**, 339—344. Compare *Pharm. Rundschau*, 1890, **8**, 29; A., 1901, ii, 679).—The author traverses the statements made by Kobert (preceding abstract) as regards the toxicity, glucosidolytic activity, and milk-clotting property of "robin." Repetition of some of his previous experiments with a sample of "robin" prepared in 1904 shows that the material is still poisonous, and is capable of hydrolysing sinigrin and amygdalin.   T. A. H.

Hydrogen Cyanide in Salt-Grass (Triglochin). JAN J. BLANKSMA (*Pharm. Weekblad*, 1913, **50**, 1295—1302. Compare Greshoff, *ibid.*, 1908, **45**, 1167).—Greshoff's observation of the occurrence of hydrogen cyanide in salt-grasses is confirmed. The proportion is highest in the flowers and young fruit, and falls off as the fruit ripens. These grasses contain no acetone, but

maceration with water produces ethyl alcohol and acetaldehyde, even from varieties not containing hydrogen cyanide. The mode of combination of the hydrogen cyanide in the grasses is a matter of doubt. A. J. W.

The Presence of a Nitrogenous Substance in the Seedlings from Vicia Faba. TORQUATO TORQUATI (*Chem. Zentr.*, 1913, ii, 517—518; from *Arch. Farm. sperim.*, 1913, **15**, 213—223).—A *substance* of the approximate formula $C_{11}H_{15}O_5N$, m. p. 273—275°, was isolated from the seedlings in the following way. The disintegrated material was extracted with hot water acidified with acetic acid. The proteins and pectins were separated from the filtrate by lead acetate. The filtrate from these, on neutralisation with ammonia, yielded a light yellow precipitate. This was decomposed with hydrogen sulphide, and a substance precipitated from the solution thus obtained by basic lead acetate. On decomposing the precipitate thus formed by hydrogen sulphide and concentration of the solution, the above-mentioned substance separated in crystalline form. The substance is neutral and rapidly darkens, especially in the presence of alkalis. With potassium ferrocyanide and ammonia it yields a ruby-red solution, which rapidly darkens. Permanganate is quickly reduced by it in acid solution, and it also reduces various mercuric, silver, and copper salts. S. B. S.

The Presence of a Nitrogenous Substance in the Green Pods of Vicia faba. TORQUATO TORQUATI (*Chem. Zentr.*, 1913, ii, 518; from *Arch. Farm. sperim.*, 1913, **15**, 308—312).—In addition to tyrosine, discovered by Bourquelot and Hérissey, the author has succeeded in obtaining the same chromogenic substance as that got by him from the seedlings (see preceding abstract). This substance is not contained in the seeds themselves nor in the pods of *Pisum*.

S. B. S.

Calcareous Chlorosis of Green Plants. Rôle of the Root Excretions in the Absorption of Iron from Calcareous Soils. PIERRE MAZÉ, M. RUOT, and M. LEMOIGNE (*Compt. rend.*, 1913, **157**, 495—498. Compare A., 1912, ii, 1088).—The chlorosis, which is induced in plants grown in water cultures containing an excess of calcium carbonate in suspension or soluble calcium salts in solution, can be destroyed by the addition of small quantities of organic acid to the culture solutions, the green colour returning to the leaf. The appearance of chlorosis is accompanied by a pink coloration of the culture liquid, and this gradually disappears after the addition of the acid. W. G.

[**The Lime-Magnesia Ratio.**] JOHN A. VOELCKER (*J. Roy. Agric. Soc.*, 1912, **73**, 325—358).—Wheat was found to be benefited by the addition of magnesia to soil in which magnesia is deficient, provided that the magnesia does not exceed the lime. An excess of magnesia over lime has a toxic effect, and diminishes the yield. Addition of lime will then be beneficial, and an excess of lime does not possess the toxic effect which magnesia in excess has.

Both magnesia and lime are capable of modifying the growth of wheat, and altering the character of the root and the composition of the grain. N. H. J. M.

[**Influence of Lithium, Zinc and Lead Salts on Wheat.**] JOHN A. VOELCKER (*J. Roy. Agric. Soc.*, 1912, 73, 314—325. Compare A., 1911, ii, 922).—The results of pot experiments showed that lithium salts are toxic when the soil contains 0·003% or more of lithium, whilst amounts not exceeding 0·002% have a stimulating effect. The best results are obtained with the nitrate (which is the most stimulating, as well as the most toxic of the different salts) when the amount of lithium does not exceed 0·001%.

Zinc salts have a slightly stimulating action on wheat when the soil contains less than 0·02% of zinc. Larger amounts of zinc have a toxic action.

Lead salts have no toxic effect when the soil contains as much as 0·03% of lead. The nitrate seems to have a stimulating effect.

It is worthy of note that much larger amounts of zinc than of lithium may be present in the soil without having any injurious action on wheat, the relative amounts being 10 : 1.

As regards the period in which the stimulating action takes place, the results so far obtained seem to indicate that it is during the germination of the seed rather than later. The action may result in considerable alterations in the development of the plant, in root production, and even in the character of the grain. N. H. J. M.

The Conditions which Affect the Activity of the Amylolytic Enzymes in Wheat Flour. C. O. SWANSON and JOHN W. CALVIN (*J. Amer. Chem. Soc.*, 1913, 35, 1635—1643).—It is known that flour when mixed with water and allowed to digest for four hours at 60° shows great diastasic activity. The results of this investigation show that the optimum temperature for the production of the maximum amount of reducing sugars is near 65°, and that the best proportions of flour and water lie between 1 : 4 and 1 : 10, little difference being observable between these limits. The transformation is mainly effected in the first hour (approx. 88% of the total change), and under favourable conditions more than two-fifths of the flour undergoes conversion into soluble substances (calculated as maltose). Small quantities of sulphuric acid, sodium hydroxide, dipotassium hydrogen phosphate, and sodium chloride all exert an inhibitory effect on the action of the enzymes of the flour, the influence being most marked with sodium hydroxide, and least with sodium chloride. Although little difference is observable between the quantities of reducing sugars formed in the action of water on various grades of flour from the same wheat, the inhibitory effect of the chemicals named is less marked with a low grade than with a straight flour. D. F. T.

The Amounts of Sulphur and Chlorine in the Rice Plant. ALICE R. THOMPSON (*J. Amer. Chem. Soc.*, 1913, 35, 1628—1634).— An investigation on the effect of fertilisers on the sulphur and

chlorine content of the plant grown in natural soil conditions and in sand cultures. The plant was analysed before flowering, the foliage and roots being examined separately; a second examination was made of the panicles, leaves, stems, and roots at the flowering period, and a third was made of the chaff, grain, leaves, stems, and roots at maturity. Analysis was also made of the soil of the rice field and of the water supplied.

The results of the analyses are tabulated in the original.

D. F. T.

Relationship between the Weight of the Sugar Beet and the Composition of its Juice. J. ARTHUR HARRIS and ROSS A. GORTNER (*Biochem. Bull.*, 1913, **2**, 524—529).—The wide-spread belief that large beets contain less sugar % than small beets is shown to rest upon very slender foundations.　　　　W. D. H.

The Influence of Growth in the Shade on the Various Constituents of Tobacco. ALBERT STUTZER and SAMUEL GOY (*Biochem. Zeitsch.*, 1913, **56**, 220—229).—Comparisons were made of the nicotine and potassium contents of the leaves from plants which were grown in pots in the shade, and from those grown under similar conditions in direct sunlight. There was less organic matter in those grown in the shade, but the percentages of nitrogen were higher. Both series of plants were richly fed with urea nitrate. In the lower leaves from the shaded plants the amount of nicotine was both absolutely and relatively higher than in the leaves of the other plant. In the upper leaves, however, the relative percentage of nitrogen in the form of nicotine in the shaded plants was less than that in the unshaded. The dried material of the shaded plants contained more potassium than that of the unshaded.

S. B. S.

Lævulose in the Leaves of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 428—430).— By dialysis of the leaves of this tobacco, the author has isolated a sugar which was identified as lævulose by means of its phenyl-glucosazone, rotatory power, and other properties.　　　R. V. S.

The Ferments of Plants of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 431—437).— A glycerol extract of the green leaves of this tobacco appears to contain oxydases, peroxydases, catalases, invertase, amylases, lipases, emulsin, and proteolytic ferments.　　　R. V. S.

Titanium and Rare Metals in the Ashes of Leaves of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 437—440).—In the leaves of this tobacco, the author has detected lithium, cæsium (both spectroscopically), titanium (spectroscopically and by colour reactions), and barium, as well as the other elements previously found in this plant.

R. V. S.

The Ethereal Extract of the Leaves of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 440—445).—That portion of the substances extracted with ether which is insoluble in cold alcohol yields a white *substance*, m. p. 62—63°, which gives the Liebermann-Burchard reaction for the ethers of the sterols, and contains 8·54% of oxygen (compare Thorpe and Holmes, T., 1901, **79**, 982). The resin of the leaves is a substance of high molecular weight (690), which yields a bromo-derivative, m. p. 118° (decomp.), and contains 64·89% of bromine but no oxygen. Oxidation of the resin with nitric acid yields a *substance*, $C_8H_{12}O_4$, m. p. 55—56°, possibly a hexahydrophthalic acid. Its *ammonium* salt yields colloidal solutions of a very typical character.   R. V. S.

First Results of Manuring Vines with Manganese Sulphate. F. A. SANNINO and A. TOSATTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 237—242).—In one year's experiment the yield was considerably increased (possibly owing to the added sulphate), but the dextrose of the product was less than in the case of the unmanured vines, and the acidity was greater. In the second year the increase in yield was not so marked, and the dextrose and acid were present in about normal amounts. Details are given of the testing of the wines made from the manured and from the unmanured vines.

                                                        R. V. S.

Typical Peats. HERMANN MINSSEN (*Landw. Jahrb.*, 1913, **44**, 269—330).—A comprehensive study of different kinds of peat obtained from many localities, by which the author attempts to draw up a classification. Two great groups of peat formation are indicated, that is, the peats of "high" bogs and those in "low" positions, and between these many minor types exist. The different plants of which peats are formed are studied, and the results of numerous analyses tabulated, with a discussion on the possible significance of the facts observed.   F. M. G. M.

Manurial Experiments with Calcium Cyanamide, Sodium Nitrate, and Ammonium Sulphate on Sand and Peat Soils. BRUNO TACKE and FR. BRÜNE (*Landw. Versuchs.-Stat.*, 1913, **83**, 1—100).—Frank's calcium cyanamide and Polzeniuss's calcium cyanamide (which contains calcium chloride) give similar results on sandy soils. On peaty soil the latter only had 81% of the value of Frank's manure.

Calcium cyanamide should be applied not with the seed, but at least a week beforehand; and it should at once be harrowed in. Different crops show different degrees of sensitiveness; rye being more sensitive than oats and potatoes when the manure is applied as top dressing, whilst oats is specially liable to injury when the manure is applied at the same time as the seed. As regards the utilisation of nitrogen, calcium cyanamide was far behind ammonium sulphate and sodium nitrate.   N. H. J. M.